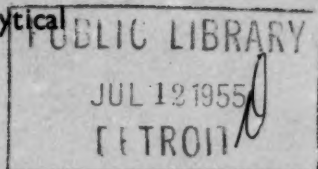


TECHNOLOGY DEPT.

RR

ANALYTICAL ABSTRACTS

Dealing with all branches
of Analytical Chemistry:
Published Monthly with
THE ANALYST by the
Society for Analytical
Chemistry



Editor: NORMAN EVERS, B.Sc., Ph.D., F.R.I.C.
20, EASTCHEAP, LONDON, E.C.3
Telephone: MANSION House 6608

Published for the Society by
W. HEFFER & SONS, LTD., CAMBRIDGE, ENGLAND

Volume 2

Price 4s.

Subscription Rate, inclusive of Index, 50s. per annum, Post Free

No. 6, Abstracts 1426-1717

June, 1955

Binding...

W. Heffer & Sons Ltd. announce that they are now able to BIND copies of ANALYTICAL ABSTRACTS, in an approved binding case, at a cost of 9/- per volume. The 12 Parts for 1954 together with Index and remittance for 9/- should be sent to

**W. HEFFER & SONS, LIMITED
HILLS ROAD, CAMBRIDGE**

PRICE OF ANALYTICAL ABSTRACTS

Subscription Rate, inclusive of
Index 50s. per annum, post free.

Abstracts printed on one side
of the page only, exclusive
of Index 60s. per annum, post free.

The subscription rate for *The Analyst* together with *Analytical Abstracts* and Indexes is 80s. per annum, post free.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 7-8, Idol Lane, London, E.C.3. Telephone: MANsion House 6608.

ANALYTICAL ABSTRACTS



LATEST
PUBLICATION

A new edition

Hopkin & Williams Ltd. announce a new edition of "Organic Reagents for Metals". This publication, which was first issued in 1933, now appears under the title "Organic Reagents for Metals and other Reagent Monographs", 5th edition. Volume 1, which is now available, consists of twenty-seven Monographs, fourteen of which have already been issued individually, the remaining thirteen Monographs appearing for the first time in this volume. Following the publication of Volume 1, a further series of individual Monographs will be issued from time to time and these will eventually appear in a collective form as Volume 2.

"Organic Reagents for Metals and other Reagent Monographs" 5th Edition Vol. 1 (1955) 15/- nett, post free.

**HOPKIN
& WILLIAMS
LIMITED**

Manufacturers of Fine Chemicals
for Research and Analysis.
CHADWELL HEATH, ESSEX, ENGLAND

RECENT CATALOGUES*

*No. 675: Books on the History of Science and Technology: Antiquarian, Second-hand and New, English and Foreign.
54 pp.

*No. 676: Forthcoming Scientific and Technical Books: a select list.
22 pp.

*Catalogues gratis on application

W. HEFFER & SONS
LIMITED

Petty Cury · Cambridge
England

*You can make no mistake
in employing*

WHATMAN

FILTER PAPERS

The makers have perfected a range covering the special requirements of every industry.

- QUALITATIVE GRADES
- EXTRACTION THIMBLES
- SINGLE and ACID WASHED QUALITIES
- HARDENED FILTER PAPERS
- SPECIALITIES

STOCKED BY ALL LABORATORY FURNISHERS

Made by:—

W. & R. BALSTON LTD., MAIDSTONE, KENT.

Sole Sales Agents:—

H. REEVE ANGEL & Co. Ltd., 9, BRIDWELL PLACE
LONDON, E.C.4.

American Men of Science

A BIOGRAPHICAL DIRECTORY

Ninth Edition

Edited by Jaques Cattell

In Three Volumes

Vol. I. The Physical Sciences. 2180 pages. Imp. 8vo., strongly bound in buckram. £7 10s. 0d.

Vol. II, Biological Sciences, is due this Autumn, and Vol. III, Social Sciences, in the Spring of 1956. Their prices will be announced later; the volumes are expected each to be a little more than half the size of Volume I.

This first volume contains 43,518 entries, each giving a brief account of scientists' appointments and particular lines of work.

Available from

W. HEFFER & SONS LTD.

ENGLISH AND FOREIGN BOOKSELLERS

3-4, PETTY CURY · CAMBRIDGE · ENGLAND

Telephone 58351

Telegrams: "Heffer, Cambridge"

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1426. Universal-indicator papers for the pH range 0 to 11. F. Čuta and K. Kámen (*Chem. Listy*, 1954, **48** [5], 669-673).—Two varieties of universal-indicator papers for estimating pH in the range 0 to 11 have been prepared and their properties tested. The composition of the impregnating soln. (in g per litre of methanol) is: hexamethoxyl red, 2.000; methyl orange, 0.018; methyl red, 0.035; bromothymol blue, 0.750; phenolphthalein, 0.320. The colour changes from red - violet (at pH 0) via orange, yellow and green to violet - blue (at pH 11). The second soln. contains (in g per litre of methanol): tropaeolin OO, 0.220; dimethyl yellow, 0.220; bromocresol green, 0.070; bromothymol blue, 0.750; phenolphthalein, 0.320. The colour changes from violet - red (at pH 0) via orange, yellow and green to blue - black (at pH 11). For either, the average error is ± 0.3 to 0.4 pH unit. G. GLASER

1427. A new argentimetric adsorption indicator: Brilliant Yellow. J. Bognár and J. Vereskői (*Acta Chim. Hung.*, 1954, **5** [1-2], 91-96).—A 0.5 per cent. soln. of Brilliant Yellow is a sensitive indicator for the titration of halide or thiocyanate ions, even at a dilution of 0.0005 N. The colour change is from lemon - yellow to orange - red in the presence of excess of Ag^+ for acid and neutral soln., and from orange - red to violet for alkaline soln. All the ions may be titrated in neutral and acid soln., provided that the pH is > 2 , but the titration of Cl^- is possible only if the soln. is diluted to 50 per cent. with alcohol or acetone. I^- may also be titrated in ammoniacal soln., provided that the ion concn. of aq. NH_3 is < 0.1 N. The presence of other electrolytes has no effect on the titration, except in the case of Cl^- . If the titration is reversed so as to determine the Ag^+ , the indicator does not give a satisfactory colour change, and an indirect method must be used. J. H. WATON

1428. Improvement in the precipitating power of reagents by increasing the cyclocomplex-forming groupings. V. M. Dziomko (*Sb. Statef Vses. Zaoch. Politekh. In-ta*, 1953, **5**, 105-109; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 34,631).—Reagents having only one cyclocomplex-forming group ("mono"-reagents) are less efficient as precipitants than "bis"- or "tri"-reagents. The precipitating power of some "bis"-reagents for Al^{+++} , Cu^{++} , Ni^{++} , Fe^{+++} and Mn^{++} is investigated, viz., 8:8'-dihydroxy-5:5'-diquinolylmethane, 8:8'-dihydroxy-5:5'-diquinolylphenylmethane, 7:7'-dibromo-8:8'-dihydroxy-5:5'-diquinolylmethane, 1:1'-dichloro-2:2'-di-(8-hydroxy-5-quinolyl)ethylene, 5:5'-dimethyl-8:8'-dihydroxy-7:7'-diquinolylmethane, 5:5'-dimethyl-8:8'-dihydroxy-7:7'-diquinolyl sulphide and 8:8'-dihydroxy- α - α -diquinolyl sulphide. The precipitating power of these reagents is greater than that of the corresponding "mono"-reagents (8-hydroxyquinoline and its derivatives) and the

complexes formed are insoluble in chloroform, carbon tetrachloride, benzene and pentanol.

E. HAYES

1429. Titrations with extractive end-points. I. The permanganate titration. N. A. Gibson and R. A. White (*Anal. Chim. Acta*, 1955, **12** [2], 115-123).—Triphenylmethylarsonium permanganate is readily extracted from aq. soln. by CHCl_3 , CCl_4 or 1:2-dichloroethane. This provides a means of end-point detection when permanganate titrations are performed in the presence of coloured ions. Suitable volumes of 5 per cent. aq. triphenylmethylarsonium chloride and purified 1:2-dichloroethane are added to the soln. to be titrated, the flask is shaken, after each addition of permanganate, and the organic layer is observed in a short side-arm near the base of the flask. The layer is red - purple at the end-point. The method is applied to the titration of Fe^{++} , AsO_3^{+++} and oxalate with 0.1 N to 0.01 N KMnO_4 and in the presence of coloured ions in large excess. It is also applied to the determination of phosphite, I^- , IO_3^- , formate and glycerol by the addition of alkaline KMnO_4 soln. in excess and the titration of the excess in acid soln. with 0.1 N oxalic acid. Results are in good agreement with those obtained by potentiometric titration.

W. C. JOHNSON

1430. The analytical properties of 8-hydroxy-5-, -6- and -7- trifluoromethylquinoline[s]. R. Belcher, A. Sykes and J. C. Tatlow (*J. Chem. Soc.*, 1955, 376-380).—8-Hydroxy-5-, 6-, and 7-trifluoromethylquinolines are tested by reaction with metal ions at 80°C for 15 min. in solutions A (acetic acid - sodium acetate), B (aq. NH_3 soln. - ammonium acetate - Na K tartrate) and C (NaOH - Na K tartrate) (Irving *et al.*, *J. Chem. Soc.*, 1949, 1497); the 7- CF_3 compound gives no precipitates. Sensitivity limits have been determined for the 6- CF_3 and 5- CF_3 compounds with a number of metal ions in the three solvents. The acid dissociation constants of the 5- and 6- CF_3 isomers are measured and are in accord with complexing power, but the anomalous behaviour of the 7- CF_3 isomer is probably due to ortho effects. The possible effect of the basic character of the N atom in the different compounds is discussed.

E. J. H. BIRCH

1431. Some factors influencing the precision of nephelometric methods. New reagents for the investigation of some impurities. E. H. Vogelenzang (*Pharm. Weekbl.*, 1955, **90** [4], 138-144).—The optical effect (intensity of the scattered light) of a suspension increases with the size of the particle up to approx. the wavelength of light and then decreases according as the observed effect depends upon reflection or scattering. The scattering of the light also depends upon refractive index difference so that foreign dissolved salts may make a large difference. The solubility of the suspended particles depends upon the ionic strength sufficiently to falsify the results and on size of crystals of the disperse phase; the latter effect also depends upon the surface

tension of the suspended particles. These phenomena interfere with nephelometric comparison of ppt. of BaSO_4 , Ca oxalate or MgNH_4PO_4 , when these are used as limit tests for impurities in drugs. Reagents are suggested which already contain a number of crystals of the appropriate suspension to ensure the necessary degree of supersaturation and avoid the formation of spontaneous and irregular nuclei. Formulations of solutions of H_2SO_4 (for Ba), ammonium oxalate (for Ca), $\text{Na}_2\text{HPO}_4 \cdot \text{NH}_3$ (for Mg), $\text{Na}_2\text{Co}(\text{NO}_2)_6$ (for K) and $\text{Ba}(\text{NO}_3)_2$ (for sulphate) are given. E. J. H. BIRCH

1432. Effect of potassium bromide content of developer in reducing development "macro-errors." T. Török (*Magyar Kém. Foly.*, 1953, **59** [6], 191-192; *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 36,374).—Photographic inaccuracies in spectral analysis are due to inhomogeneous emulsion sensitivity ("micro-errors") ± 1.5 to 3.5 per cent. and to uneven development ("macro-errors" of up to 20 per cent.). These errors affect determinations of the relative intensities of spectral lines. Uneven development is due to differences in the rates of diffusion exchange of oxidation products, gelatin and the developing-liquid. Photographic errors are reduced by increasing the potassium bromide content of the developer. E. HAYES

1433. Effects of inert gases on d.c. arc discharge. B. L. Vallee and S. J. Adelstein (*J. Opt. Soc. Amer.*, 1955, **45** [1], 63).—By using an interrupted arc in which the sample is not fully consumed during the arcing period and where the time of arcing is adjusted to constant background, it is found that: (i) when helium is used in place of air, lines of the first ionisation are enhanced relative to those of the neutral atom; and (ii) with argon, volatilisation is prolonged, which results in the enhancement of many lines, including ultimate lines. The experimental arrangements used by Stone (*Anal. Abstr.*, 1954, **1**, 2611) precluded his verification of the second observation. B. S. COOPER

1434. Basic theory and fundamentals of fluorescent X-ray spectrographic analysis. H. Friedman, L. S. Birks and E. J. Brooks (*A.S.T.M. Symp. on Fluorescent X-ray Spectrogr. Anal.*, 1954, 3-26).—The principles of X-ray excitation and the construction of several types of X-ray spectrographs are described. The calculation of spectral intensities by means of Geiger, proportional and scintillation counters is discussed, and applications are given. By increasing the counts, low intensities can be measured. The method is not suited to the determination of elements of low at. number; possible developments to overcome this disadvantage are indicated. Absolute quant. analysis is possible, but involves complicated corrections; in the usual method comparison standards are used. METALL. ABSTR.

1435. Electrochemical methods of analysis. Principles and applicability. J. Smelik (*Prakt. Chem.*, 1954, **5** [6], 133-134, 253-255).—A review is presented of potentiometric and polarographic methods. (48 references.) A. R. PEARSON

1436. Potentiometric titrations with controlled-current input. R. N. Adams (*Anal. Chem.*, 1954, **26** [12], 1933-1938).—Current-scanning polarography technique is extended to an electrometric titration analogous to conventional amperometry. A small controlled current from a 1.5-V dry cell with 1 to 5-megohm resistor is applied to a polarographic

electrode and a reference half-cell. Resultant polarographic voltages are followed by a continuous-indicating pH meter or vacuum-tube voltmeter, as a function of the vol. of titrant added. Zn is titrated satisfactorily with ferrocyanide. As^{III} is titratable with bromate-bromide in HCl by using platinum foil in a stirred solution to speed up the slow reaction near the end-point. The new method is no better than conventional potentiometry for titrating Fe^{II} with Ce^{IV} . Results are interpreted in terms of experimental polarograms and the uselessness of theoretical polarograms is emphasised. Cd can be titrated satisfactorily with ethylenediaminetetra-acetic acid at the dropping-mercury electrode, on allowing for decreasing current level during the titration. In general, the current-input method gives larger breaks than classical potentiometry only when one of the polarographic systems involved is the background medium; optional use of cathodic or anodic current is afforded. D. R. GLASSON

1437. Study of the mechanism of high-frequency titration by means of a Q-meter. M. Honda, K. Nakano and A. Satuka (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [12], 1299-1302).—The mechanism of high-frequency titration with a titrimeter of receiver-coil type is studied by use of a Q-meter. The apparent Q-value (the reading of the Q-meter) is plotted against the capacity of the circuit for different concn. of HCl. When the concn. of HCl is increased, the capacity at which the tuning is obtained is decreased. The real Q-value (at the tuning point) shows at first a min., then a max., and decreases once again with the increase of HCl concn. These relations can be expressed clearly with a three-dimensional diagram, which can account for a variety of observations of the authors and other workers. The considerations which were shown to be valid for the elucidation of the mechanism of an oscillation-type titrimeter (Nakano, *J. Chem. Soc. Japan*, 1954, **75**, 776) are applied to the present results and found to conform with them. K. SAITO

1438. Studies on the preparation of material for the measurement of radioactivity. K. Kimura, N. Saito, T. Tachibana, J. Osawa and O. Shibata (*Japan Analyst*, 1953, **2** [2], 92-96).—To obtain a reproducible geometrical distribution of material on a dish for radioactivity measurement, the application of artificial resin to the surface of the dish is studied. To avoid the creeping of the liquid and to ensure a uniform distribution of the residue on the surface after the evaporation of the solvent, treatment with methyl methacrylate resin is the most suitable. The inside surface of the dish, except the central part of the bottom, is lined with a benzene soln. of the resin and the benzene is then evaporated off at room temp. The method of the evaporation of the sample soln. on the dish was studied with other resins and the results were statistically analysed. K. SAITO

1439. Use of coupled columns in chromatography. L. Hagdahl (*Science Tools*, 1954, **1** [3], 21-28).—Factors influencing the blurring of the eluate fronts are discussed. Frontal blurring is minimised by the use of finely powdered adsorbents and low rates of flow, but homogeneous packing is then difficult and leads to frontal deterioration. Effective chromatographic separations in single columns are thus restricted to low concn., i.e., with small amounts of material. Coupled columns transform sharp but deteriorated fronts into diffuse fronts in

the narrow channels collecting the flow before deterioration becomes too serious; these diffuse fronts are progressively sharpened by pressing through other columns of vol. consistently decreasing in the direction of flow. The separation capacity of the series is the sum of the individual column capacities, but the sharpness of the emerging front is that of the smallest column; the principle is best applicable at higher concn. Reshaping of diffuse fronts is normally achieved with column-size ratios of 2, e.g., 1, 2, 4, 8 and 16 ml, which accords with the convexity of most sorption isotherms. Elution and gradient-elution analyses are also improved by coupled columns. Effects of high pressures and corrosion by solvents are avoided by constructing the columns of steel lined with polyethylene or Teflon. Applications include improved separation of glucose, sucrose and raffinose with ephehrine displacer; of normal unbranched fatty acids on activated carbon; and of displacement analysis using ion exchangers.

D. R. GLASSON

1440. Composite column for chromatography. Anon. (*Science Tools*, 1954, **1**, 28).—A series of columns and associated components has been designed for chromatography with coupled columns (*Anal. Abstr.*, 1955, **2**, 1439). It includes six columns of the following volumes: 0.5, 1, 2, 4, 8 and 16 ml. There is a special coupling for use in conjunction with a continuous analyser. Each part is made of acid-proof steel lined with polyethylene.

A. M. SPRATT

1441. Circular-paper chromatography in qualitative analysis. J. G. Surak and R. J. Martinovich (*J. Chem. Educ.*, 1955, **32** [2], 95-98).—Experimental details are given for the separation of cations of analytical groups I, II, III, IV and V. The complete analysis described can be easily completed in 1 hr.

A. LEDWITH

1442. Gas-phase chromatography. A. E. Martin and J. Smart (*Nature*, 1955, **175**, 422-423).—The detection of organic gases and vapours eluted from a chromatographic column of activated carbon, by a stream of nitrogen, is improved by passing the mobile phase through a tube of heated CuO at $\approx 750^\circ\text{C}$. The products of combustion are then passed into an infra-red analyser that is sensitive only to CO_2 . Water vapour does not interfere, but large amounts of water formed in combustion must be removed to prevent undue loss of CO_2 . The increased sensitivity to any organic gas after combustion is proportional to the number of carbon atoms in the original molecule. For each gas there is an optimum absorption-cell length; the cell volume should be approximately equal to the volume of gas required to elute the gas from the apparatus.

D. G. HIGGS

1443. Quantitative chromatography on treated paper. I. Preparation of paper for the determination of anions. A. Murata (*J. Chem. Soc. Japan*, 1954, **75** [8], 827-831).—The conditions for the prep. of filter-paper impregnated with Al_2O_3 , which is used for the quant. chromatography of anions, are precisely studied. The more Al_2O_3 contained in the paper, the less is the width of bands caused by adsorption of anions. The sensitivity of the paper is adjusted by changing the concn. of the initial Na_2AlO_3 soln. or of HClO_4 . *Recommended procedure*—Filter-paper of a uniform quality is treated with 0.5 M Na_2AlO_3 soln. (made from Al and NaOH), containing an excess of 0.2 M NaOH, for 10 min. and dried at 100°C . It is washed thoroughly

with water, put in 0.003 to 0.01 M HClO_4 for 10 min. and dried without washing at room temp. The paper thus prepared attains stability in one week, and then remains unaltered. Bands of MoO_4^{2-} and $\text{Fe}(\text{CN})_6^{4-}$ were examined and the width was found to be proportional to the concn. of the anion (10^{-8} mole).

K. SAITO

1444. Use of triethylammonium buffers in ion-exchange chromatography and electrophoresis. [Preliminary communication.] J. Porath (*Nature*, 1955, **175**, 478).—Triethylammonium formate, acetate, bicarbonate and carbonate buffers are advocated for preparative ion-exchange chromatography or electrophoresis, as the required pH can be obtained. These buffers are volatile and can be removed by lyophilisation, they do not interfere with u.v. absorption nor with many reactions, including that of ninhydrin, and they are stable to oxidation.

E. J. H. BIRCH

1445. Chromatography on paper impregnated with ion-exchange resins. A preliminary report. M. Lederer (*Anal. Chim. Acta*, 1955, **12** [2], 142-145).—Filter-paper is impregnated with ion-exchange resins by dipping it in an aq. suspension of a "colloidal" form of the resin. The impregnated papers are used for the chromatographic separation of some rare earths. Co, Cu and Fe^{3+} are separated by partition chromatography on paper impregnated with Dowex-50 cation-exchange resin with the use of acetone-HCl-water, but plain filter-paper gives a similar result. Paper impregnated with Dowex-2 anion-exchange resin demonstrates the sequence changes of Co, Cu and Fe with variation in the concn. of the aq. HCl used as eluent.

W. C. JOHNSON

1446. Reactions of some Lewis acids with a series of simple basic indicators in aprotic solvents. D. L. Hawke and J. Steigman (*Anal. Chem.*, 1954, **26** [12], 1989-1992).—The reactions of a large number of Lewis acids (Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1147) with a series of uncharged basic indicators were qual. examined in the solvents benzene, chlorobenzene and chloroform. A qualitative order of acidity was established, which was similar to the order of catalytic activity reported for several Friedel-Crafts reactions. The reaction between anthraquinone and AlBr_3 in chlorobenzene was examined spectrophotometrically and it was concluded that the AlBr_3 could react with one or both O atoms in the anthraquinone. G. P. COOK

2.—INORGANIC ANALYSIS

1447. Chromatographic separation of inorganic ions on specially prepared calcium sulphate sticks. Binayendra Nath Sen (*Anal. Chim. Acta*, 1955, **12** [2], 154-157).—Calcium sulphate sticks 6 to 8 in. in length by 6 to 8 mm in diameter are cast from a mixture of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and plaster of Paris (11 + 9) moistened with water. The sticks are dried for ≈ 4 hr. at a temp. 5°C above atm. temp. and for 1 week in dry air at atm. temp. A stick is placed in a test-tube containing 3 to 4 ml of water, or water acidified with dil. HCl, and a spot (1 to 2 drops) of a soln. of salts is applied 1 to $1\frac{1}{2}$ in. above the liquid level. When the liquid has risen well above the spot, the stick is held in a stream of H_2S or is sprayed with a suitable reagent. Cu^{II} is separated from Sb^{III} , As^{III} , Hg^{II} or Fe^{III} ; Bi^{III} from Sb^{III} or As^{III} ; Cd^{II} from Sb^{III} or Sn^{II} ; and Hg^{II} from As^{III} or Sb^{III} .

W. C. JOHNSON

tension of the suspended particles. These phenomena interfere with nephelometric comparison of ppt. of BaSO_4 , Ca oxalate or MgNH_4PO_4 , when these are used as limit tests for impurities in drugs. Reagents are suggested which already contain a number of crystals of the appropriate suspension to ensure the necessary degree of supersaturation and avoid the formation of spontaneous and irregular nuclei. Formulations of solutions of H_2SO_4 (for Ba), ammonium oxalate (for Ca), $\text{Na}_2\text{HPO}_4 \cdot \text{NH}_3$ (for Mg), $\text{Na}_2\text{Co}(\text{NO}_2)_6$ (for K) and $\text{Ba}(\text{NO}_3)_2$ (for sulphate) are given. E. J. H. BIRCH

1432. Effect of potassium bromide content of developer in reducing development "macro-errors." T. Török (*Magyar Kém. Foly.*, 1953, **59** [6], 191-192; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 36,374).—Photographic inaccuracies in spectral analysis are due to inhomogeneous emulsion sensitivity ("micro-errors" $\approx \pm 1.5$ to 3.5 per cent.) and to uneven development ("macro-errors" of up to 20 per cent.). These errors affect determinations of the relative intensities of spectral lines. Uneven development is due to differences in the rates of diffusion exchange of oxidation products, gelatin and the developing-liquid. Photographic errors are reduced by increasing the potassium bromide content of the developer. E. HAYES

1433. Effects of inert gases on d.c. arc discharge. B. L. Vallee and S. J. Adelstein (*J. Opt. Soc. Amer.*, 1955, **45** [1], 63).—By using an interrupted arc in which the sample is not fully consumed during the arcing period and where the time of arcing is adjusted to constant background, it is found that: (i) when helium is used in place of air, lines of the first ionisation are enhanced relative to those of the neutral atom; and (ii) with argon, volatilisation is prolonged, which results in the enhancement of many lines, including ultimate lines. The experimental arrangements used by Stone (*Anal. Abstr.*, 1954, **1**, 2611) precluded his verification of the second observation. B. S. COOPER

1434. Basic theory and fundamentals of fluorescent X-ray spectrographic analysis. H. Friedman, L. S. Birks and E. J. Brooks (*A.S.T.M. Symp. on Fluorescent X-ray Spectrogr. Anal.*, 1954, 3-26).—The principles of X-ray excitation and the construction of several types of X-ray spectrographs are described. The calculation of spectral intensities by means of Geiger, proportional and scintillation counters is discussed, and applications are given. By increasing the counts, low intensities can be measured. The method is not suited to the determination of elements of low at. number; possible developments to overcome this disadvantage are indicated. Absolute quant. analysis is possible, but involves complicated corrections; in the usual method comparison standards are used. METALL. ABSTR.

1435. Electrochemical methods of analysis. Principles and applicability. J. Smelik (*Prakt. Chem.*, 1954, **5** [6], 133-134, 253-255).—A review is presented of potentiometric and polarographic methods. (48 references.) A. R. PEARSON

1436. Potentiometric titrations with controlled-current input. R. N. Adams (*Anal. Chem.*, 1954, **26** [12], 1933-1938).—Current-scanning polarography technique is extended to an electrometric titration analogous to conventional amperometry. A small controlled current from a 1.5-V dry cell with 1 to 5-megohm resistor is applied to a polarographic

electrode and a reference half-cell. Resultant polarographic voltages are followed by a continuous-indicating pH meter or vacuum-tube voltmeter, as a function of the vol. of titrant added. Zn is titrated satisfactorily with ferrocyanide. As^{III} is titratable with bromate-bromide in HCl by using platinum foil in a stirred solution to speed up the slow reaction near the end-point. The new method is no better than conventional potentiometry for titrating Fe^{II} with Ce^{IV} . Results are interpreted in terms of experimental polarograms and the uselessness of theoretical polarograms is emphasised. Cd can be titrated satisfactorily with ethylenediaminetetra-acetic acid at the dropping-mercury electrode, on allowing for decreasing current level during the titration. In general, the current-input method gives larger breaks than classical potentiometry only when one of the polarographic systems involved is the background medium; optional use of cathodic or anodic current is afforded. D. R. GLASSON

1437. Study of the mechanism of high-frequency titration by means of a Q-meter. M. Honda, K. Nakano and A. Satuka (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [12], 1299-1302).—The mechanism of high-frequency titration with a titrimeter of receiver-coil type is studied by use of a Q-meter. The apparent Q-value (the reading of the Q-meter) is plotted against the capacity of the circuit for different concn. of HCl. When the concn. of HCl is increased, the capacity at which the tuning is obtained is decreased. The real Q-value (at the tuning point) shows at first a min., then a max., and decreases once again with the increase of HCl concn. These relations can be expressed clearly with a three-dimensional diagram, which can account for a variety of observations of the authors and other workers. The considerations which were shown to be valid for the elucidation of the mechanism of an oscillation-type titrimeter (Nakano, *J. Chem. Soc. Japan*, 1954, **75**, 776) are applied to the present results and found to conform with them. K. SAITO

1438. Studies on the preparation of material for the measurement of radioactivity. K. Kimura, N. Saito, T. Tachibana, J. Osawa and O. Shibata (*Japan Analyst*, 1953, **2** [2], 92-96).—To obtain a reproducible geometrical distribution of material on a dish for radioactivity measurement, the application of artificial resin to the surface of the dish is studied. To avoid the creeping of the liquid and to ensure a uniform distribution of the residue on the surface after the evaporation of the solvent, treatment with methyl methacrylate resin is the most suitable. The inside surface of the dish, except the central part of the bottom, is lined with a benzene soln. of the resin and the benzene is then evaporated off at room temp. The method of the evaporation of the sample soln. on the dish was studied with other resins and the results were statistically analysed. K. SAITO

1439. Use of coupled columns in chromatography. L. Hagdahl (*Science Tools*, 1954, **1** [3], 21-28).—Factors influencing the blurring of the eluate fronts are discussed. Frontal blurring is minimised by the use of finely powdered adsorbents and low rates of flow, but homogeneous packing is then difficult and leads to frontal deterioration. Effective chromatographic separations in single columns are thus restricted to low concn., i.e., with small amounts of material. Coupled columns transform sharp but deteriorated fronts into diffuse fronts in

the narrow channels collecting the flow before deterioration becomes too serious; these diffuse fronts are progressively sharpened by pressing through other columns of vol. consistently decreasing in the direction of flow. The separation capacity of the series is the sum of the individual column capacities, but the sharpness of the emerging front is that of the smallest column; the principle is best applicable at higher concn. Reshaping of diffuse fronts is normally achieved with column-size ratios of 2, e.g., 1, 2, 4, 8 and 16 ml, which accords with the convexity of most sorption isotherms. Elution and gradient-elution analyses are also improved by coupled columns. Effects of high pressures and corrosion by solvents are avoided by constructing the columns of steel lined with polyethylene or Teflon. Applications include improved separation of glucose, sucrose and raffinose with ephedrine displacer; of normal unbranched fatty acids on activated carbon; and of displacement analysis using ion exchangers.

D. R. GLASSON

1440. Composite column for chromatography. Anon. (*Science Tools*, 1954, 1, 28).—A series of columns and associated components has been designed for chromatography with coupled columns (*Anal. Abstr.*, 1955, 2, 1439). It includes six columns of the following volumes: 0.5, 1, 2, 4, 8 and 16 ml. There is a special coupling for use in conjunction with a continuous analyser. Each part is made of acid-proof steel lined with polyethylene.

A. M. SPRATT

1441. Circular-paper chromatography in qualitative analysis. J. G. Surak and R. J. Martinovich (*J. Chem. Educ.*, 1955, 32 [2], 95-98).—Experimental details are given for the separation of cations of analytical groups I, II, III, IV and V. The complete analysis described can be easily completed in 1 hr.

A. LEDWITH

1442. Gas-phase chromatography. A. E. Martin and J. Smart (*Nature*, 1955, 175, 422-423).—The detection of organic gases and vapours eluted from a chromatographic column of activated carbon, by a stream of nitrogen, is improved by passing the mobile phase through a tube of heated CuO at $\approx 750^\circ\text{C}$. The products of combustion are then passed into an infra-red analyser that is sensitive only to CO_2 . Water vapour does not interfere, but large amounts of water formed in combustion must be removed to prevent undue loss of CO_2 . The increased sensitivity to any organic gas after combustion is proportional to the number of carbon atoms in the original molecule. For each gas there is an optimum absorption-cell length; the cell volume should be approximately equal to the volume of gas required to elute the gas from the apparatus.

D. G. HIGGS

1443. Quantitative chromatography on treated paper. I. Preparation of paper for the determination of anions. A. Murata (*J. Chem. Soc. Japan*, 1954, 75 [8], 827-831).—The conditions for the prep. of filter-paper impregnated with Al_2O_3 , which is used for the quant. chromatography of anions, are precisely studied. The more Al_2O_3 contained in the paper, the less is the width of bands caused by adsorption of anions. The sensitivity of the paper is adjusted by changing the concn. of the initial Na_2AlO_3 soln. or of HClO_4 . *Recommended procedure*—Filter-paper of a uniform quality is treated with 0.5 M Na_2AlO_3 soln. (made from Al and NaOH), containing an excess of 0.2 M NaOH, for 10 min. and dried at 100°C . It is washed thoroughly

with water, put in 0.003 to 0.01 M HClO_4 for 10 min. and dried without washing at room temp. The paper thus prepared attains stability in one week, and then remains unaltered. Bands of MoO_4^{2-} and $\text{Fe}(\text{CN})_6^{4-}$ were examined and the width was found to be proportional to the concn. of the anion (10^{-8} mole).

K. SAITO

1444. Use of triethylammonium buffers in ion-exchange chromatography and electrophoresis. [Preliminary communication.] J. Porath (*Nature*, 1955, 175, 478).—Triethylammonium formate, acetate, bicarbonate and carbonate buffers are advocated for preparative ion-exchange chromatography or electrophoresis, as the required pH can be obtained. These buffers are volatile and can be removed by lyophilisation, they do not interfere with u.v. absorption nor with many reactions, including that of ninhydrin, and they are stable to oxidation.

E. J. H. BIRCH

1445. Chromatography on paper impregnated with ion-exchange resins. A preliminary report. M. Lederer (*Anal. Chim. Acta*, 1955, 12 [2], 142-145).—Filter-paper is impregnated with ion-exchange resins by dipping it in an aq. suspension of a "colloidal" form of the resin. The impregnated papers are used for the chromatographic separation of some rare earths. Co, Cu and Fe^{3+} are separated by partition chromatography on paper impregnated with Dowex-50 cation-exchange resin with the use of acetone - HCl - water, but plain filter-paper gives a similar result. Paper impregnated with Dowex-2 anion-exchange resin demonstrates the sequence changes of Co, Cu and Fe with variation in the concn. of the aq. HCl used as eluent.

W. C. JOHNSON

1446. Reactions of some Lewis acids with a series of simple basic indicators in aprotic solvents. D. L. Hawke and J. Steigman (*Anal. Chem.*, 1954, 26 [12], 1989-1992).—The reactions of a large number of Lewis acids (Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, 65, 1147) with a series of uncharged basic indicators were qual. examined in the solvents benzene, chlorobenzene and chloroform. A qualitative order of acidity was established, which was similar to the order of catalytic activity reported for several Friedel - Crafts reactions. The reaction between anthraquinone and AlBr_3 in chlorobenzene was examined spectrophotometrically and it was concluded that the AlBr_3 could react with one or both O atoms in the anthraquinone. G. P. COOK

2.—INORGANIC ANALYSIS

1447. Chromatographic separation of inorganic ions on specially prepared calcium sulphate sticks. Binayendra Nath Sen (*Anal. Chim. Acta*, 1955, 12 [2], 154-157).—Calcium sulphate sticks 6 to 8 in. in length by 6 to 8 mm in diameter are cast from a mixture of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and plaster of Paris ($11 + 9$) moistened with water. The sticks are dried for ≈ 4 hr. at a temp. 5°C above atm. temp. and for 1 week in dry air at atm. temp. A stick is placed in a test-tube containing 3 to 4 ml of water, or water acidified with dil. HCl, and a spot (1 to 2 drops) of a soln. of salts is applied 1 to $1\frac{1}{2}$ in. above the liquid level. When the liquid has risen well above the spot, the stick is held in a stream of H_2S or is sprayed with a suitable reagent. Cu^{II} is separated from Sb^{III} , As^{III} , Hg^{II} or Fe^{III} ; Bi^{III} from Sb^{III} or As^{III} ; Cd^{II} from Sb^{III} or Sn^{II} ; and Hg^{II} from As^{III} or Sb^{III} .

W. C. JOHNSON

1448. Separation of mixtures of tritium and hydrogen using Hertz pumps. F. J. Dunn, J. R. Mosley and R. M. Potter (*Anal. Chem.*, 1955, **27** [1], 63-64).—Separation of ^3H and ^1H is achieved either with a static train of 12 modified Hertz diffusion pumps coupled in series, or with a continuous system using 16 such pumps with the end reservoirs replaced by variable leaks. ^1H and ^3H mixtures are generated by pyrolysis (175°C) of the mixed isotope hydride of uranium, as rich in ^3H as possible. The static process produces ^1H of >99.9 per cent. purity at 5 to 8 mm pressure; the performance of the continuous system is not as satisfactory. The resulting gases are analysed by thermal-conductivity measurements (reproducibility ± 0.2 per cent.) or mass spectrometry (reproducibility ± 0.05 per cent.), after equilibration for some time at 350°C . D. A. PANTONY

1449. Improvements in and relating to quantitative determination of water. [Stabilisation of Karl Fischer reagent.] Aktiebolaget Pharmacia (Assignees of E. Blomgren and H. Jenner) (Brit. Pat. 722,983, Date Appl. 9.12.52).—The decomposition of Karl Fischer reagent with time is prevented by the addition of some of the spontaneous decomposition product to maintain equilibrium. Normally, iodide ion is produced either by adding water before standardisation or by adding pyridine hydriodide. One litre of reagent contains 84 g of I, 85 g of SO_2 , 308 g of pyridine and 690 ml of methanol and has a titre of 3.6 mg of H_2O per ml which remains constant (≈ 1 per cent.) over several months on the addition of 70 g of anhydrous pyridine hydriodide. Alternatively, 132 g of I, 97 g of SO_2 , 355 g of pyridine and 550 ml of methanol are mixed to give 1 litre of reagent, having a titre of 6.0 mg of H_2O per ml, which falls to a stabilised titre of 3.6 mg per ml on the addition of 2.4 g of water. In general, for 1.2 moles of SO_2 per litre and 3.5 moles of pyridine per litre, the ratio of I' to I₂ should be 3.2. E. J. H. BIRCH

1450. Chromatographic semi-micro analysis of gases. VI. The analysis of inert gases. J. Janák (*Coll. Czech. Chem. Commun.*, 1954, **19** [5], 917-924).—Physical data that are relevant to the chromatographic separation of the inert gases are listed and discussed. Mixtures of helium and neon can be separated from argon, argon from krypton, and krypton from xenon by this method, but helium cannot be separated from neon, nor hydrogen from helium and neon, nor nitrogen and oxygen from argon. A method is described for the determination of krypton in concentrates obtained in the liquefaction of air. The determination of small quantities of xenon in krypton and krypton in xenon is also described. In samples of krypton containing 1 per cent. and 5 per cent. of xenon, the xenon can be determined with an accuracy of 0.03 to 0.05 per cent. and 0.05 to 0.25 per cent., respectively. The corresponding figures for the determination of krypton in xenon are 0.02 to 0.04 per cent. and 0.1 to 0.3 per cent. These methods are much more rapid than those previously in common use. [This is a translation into German of a paper that was published originally in *Chem. Listy*, 1953, **47**, 1348.] M. KAPEL

1451. Quantitative analysis of mixtures of sodium, potassium, magnesium and calcium by paper chromatography. D. R. Tristram and C. S. G. Phillips (*J. Chem. Soc.*, 1955, 580-581).—Mixtures containing 4 to 40 micro-equivalents of K, Na, Ca

and Mg chlorides are chromatographed on Whatman 540 paper by the use of ethanol (plus 6 per cent. of water) for 12 to 20 hr., so that the solvent front (carrying any free HCl) passes off the paper. The strip is dried, dipped in 0.1 N AgNO_3 to precipitate all the Cl^- , and thoroughly washed. The strip is dipped in photographic developer and the revealed silver bands are washed, cut out and dissolved in 2 N HNO_3 in separate dishes, when they are titrated with 0.1 N NH_4CNS from a micro-burette. Errors of from -2.8 to $+1.6$ per cent. of the total are reported for each ion in four trials. Na and Ca separate well in spite of similar R_F values. The following mixtures have also been separated: K, Na, NH_4^+ and Li; Ba, Sr and Ca; and K, Na, Ca, Mg and Li. E. J. H. BIRCH

1452. Colorimetric determination of sodium. P. N. Kovalenko and V. V. Ten'kovtsev (*Ukr. Khim. Zh.*, 1954, **20** [4], 411-416).—The pptn. of Na as $\text{NaZn}(\text{UO}_2)_3 \cdot (\text{CH}_3\text{COO})_6 \cdot n\text{H}_2\text{O}$ from solutions containing 0.2 to 1 mg of Na per ml is 94 to 96 per cent. complete within 2 hr. when the solution contains >2 equiv. of UO_2^{++} and >6 equiv. of Zn per equiv. of Na, in 0.005 to 0.5 M H_2SO_4 . After solution of the ppt. in 0.01 to 0.7 M H_2SO_4 , NH_4CNS is added to 1.5 N, and the coloration is read after 30 min. The UO_2^{++} content is read from an empirical curve and the Na content is derived by applying a factor of 0.0339. Polarographic analysis suggests that the coloured complex is $(\text{NH}_4)_2[\text{UO}_2(\text{CNS})_4]$. R. TRUSCOE

1453. Microchemical determination of sodium in aluminium oxide and hydrated aluminium oxide with the flame photometer. A. Hegedüs, F. K. Fukker and M. Dvorszky (*Magyar Kém. Foly.*, 1953, **59** [11], 334-341; *Referativnyi Zh. Khim.*, 1954, Abstr. No. 36,400).—The flame-photometric determination of free and total Na in aluminium oxide and hydrated aluminium oxide is critically examined; the flame photometry is preceded by double electrodialysis and two treatments with dil. H_2SO_4 or HCl soln. under pressure. In the determination of 0.001 to 0.01 per cent. of Na_2O in alumina, the mean error is ± 2 per cent. In Hungarian alumina, ≈ 50 per cent. of the sodium occurs in the "bound" form. When the alumina is ignited, the "bound" Na diffuses to the surface of the corundum crystallites (especially on conversion of $\gamma\text{-Al}_2\text{O}_3$ into $\alpha\text{-Al}_2\text{O}_3$). E. HAYES

1454. Use of fluoroboric acid for the direct determination of potassium. H. M. Manasevit (*Anal. Chem.*, 1955, **27** [1], 81-83).—The effect of temp., solvent and foreign ions on the quant. pptn. of K^+ with HBF_4 is investigated. The reagent is prepared as follows: 0.5 g of NaCl is dissolved in water (40 ml) and to the soln. are added 50 per cent. HBF_4 (250 ml), 95 per cent. ethanol (500 ml) and methanol (500 ml); after cooling to 3°C , the mixture is filtered and stored in Polythene. This reagent (30 ml) is added to the sample soln. (10 ml) and the mixture is kept at 3°C for 1 hr., when it is filtered and washed with ethanol-methanol (1 + 1) and then dried at 110°C . A 25-fold excess of Na⁺ leads to an error of >1 per cent., and the method tolerates moderate excesses of Cu^{++} , Zn^{++} , Cd^{++} , Co^{++} , Ni^{++} , Mn^{++} , Fe^{+++} , Al^{+++} , Cr^{+++} , Ca^{++} , Li^+ , Mg^{++} , PO_4^{+++} and NO_3^- . These ions are also tolerated when present together, but a mixture of Ca^{++} and Al^{+++} leads to high results, as do NH_4^+ , Ba^{++} and SO_4^{--} . D. A. PANTONY

1455. **Rapid alkalimetric determination of potassium by precipitation with sodium tetraphenylboron.** H. Flaschka and H. Abdine (*Z. anal. Chem.*, 1955, **144** [6], 415-420).—A highly selective rapid and accurate determination of K is achieved by combining Kohler's procedure for the pptn. of $K[B(C_6H_5)_4]$ from mineral acid solution [*Z. anal. Chem.*, 1953, **138**, 9] with Flaschka's determination of $[B(C_6H_5)_4]'$ (*Z. anal. Chem.*, 1953, **138**, 241). The method is accurate to within 1 per cent.

D. R. GLASSON

1456. **The rapid determination of copper in iron and steel by the ammonium fluoride-iodimetric method. I. Fundamental research.** O. Kammori (*Japan Analyst*, 1953, **2** [2], 102-106).—Usatenko's NaF-iodimetric determination of Cu in iron (*Zavod. Lab.*, 1947, **13**, 116) is modified so as to be suitable for rapid (> 20 min.) analysis in a factory. Instead of NaF, the less basic NH_4F is used to make the pH adjustment easy. The undesirable influence of NO_3^- , Mn and C is also examined and eliminated as shown below. *Procedure*—The sample (1 g) is dissolved in H_2SO_4 - HNO_3 - H_2O (2:1:10) (30 ml). Saturated $KMnO_4$ soln. is dripped into the sample soln. (to decompose the carbide) until MnO_2 is pptd.; the ppt. is dissolved by adding 3 per cent. $NaNO_2$ soln. Aq. ammonia [sp. gr. 0.88 diluted (1 + 1)] is added until a ppt. of $Fe(OH)_3$ is observed; this ppt. is dissolved with 30 per cent. acetic acid (5 ml). Three per cent. $NaNO_2$ soln. (2 drops) is added to the soln. (to decomp. the higher oxide of Mn) and the excess of NO_2^- is decomposed by heating with urea (1 g). NH_4F (7 g) is added and, after cooling, Cu is titrated iodimetrically with KI (5 g).

K. SAITO

1457. **The rapid determination of copper in iron and steel by the ammonium fluoride-iodimetric method. II. The elimination of the interference of other elements and the saving of potassium iodide.** O. Kammori (*Japan Analyst*, 1953, **2** [3], 222-227).—The influence of As (< 1 per cent.), Co (< 40 per cent.), Cr (< 65 per cent.), Ni and Mo on this method (*Anal. Abstr.*, 1955, **2**, 1456) is negligible. When the content of Cr is high, a little more $NaNO_2$ should be added to complete the reduction of Cr^{VI} to Cr^{III} . No interference results when V is < 0.05 per cent., but in larger amounts V is reduced by KI to form V^{IV} and I. This effect can be eliminated by adding tartaric acid soln. (50 per cent., 2 to 5 ml) subsequent to the addition of NH_4F . A mixture of KI (1.5 g) and KCNS (4 g) can be used instead of KI (5 g).

K. SAITO

1458. **Colorimetric estimation of silver with dithizone.** L. Erdey, GY. Rády and V. Fleps (*Acta Chim. Hung.*, 1954, **5** [1-2], 133-141).—Silver can be estimated colorimetrically by extraction as its yellow dithizone complex in the presence of a large excess of other heavy metals such as Cu, Bi, Cd, Zn and Pb (but not Hg), if these are complexed with ethylenediaminetetra-acetic acid. A sodium acetate-acetic acid buffer is used to keep the acidity in the optimum range pH 4 to 5. Alternatively, the estimation may be carried out volumetrically by adding the dithizone reagent in small amounts to the buffered soln. containing Ag^+ and the complexed heavy-metal ions. After each addition, the dithizone layer is rejected, addition being continued until the reagent remains green. These methods have the advantage that the reagents and solvents used need not be free from heavy metals, although Cl^- must be absent. Ag can be estimated at a concn. of $\approx 10^{-3}$ per cent.

J. H. WATON

1459. **Determination of metals with a standard solution of potassium ferrocyanide. III. Determination of silver.** Y. Fujita and H. Kayamori (*J. Chem. Soc. Japan*, 1954, **75** [7], 653-655).— Ag^+ (10 to 500 mg in 50 ml) can be titrated slowly (one drop per 5 to 10 sec.) with $K_4Fe(CN)_6$ soln. (0.05 M) at pH 6.0 to 6.6 by use of iodine-starch soln. as internal indicator. At the end-point, AgI is decomposed by $K_4Fe(CN)_6$ to form KI, and desorbs I from the surface, which shows a blue colour with starch. Ions which form ppt. or undergo redox reactions with either Ag^+ or $Fe(CN)_6^{4-}$ should be absent.

IV. **Determination of manganese** (*Ibid.*, 1954, **75** [7], 655-658).— Mn^{2+} (3 to 50 mg in 50 ml) can be titrated (one drop per 5 to 10 sec.) in a similar way at pH 6.0 to 6.7. The end-point is shown by the disappearance of blue colour owing to the reduction of I by $Fe(CN)_6^{4-}$ to give rise to I^- and $Fe(CN)_6^{3-}$. The interference of other ions is the same as for Ag^+ .

V. **Determination of nickel** (*Ibid.*, 1954, **75** [7], 658-660).— Ni^{2+} (1 to 17 mg in 50 ml) can be titrated (one drop per 5 to 10 sec.) in a similar way to Mn^{2+} , at pH 6.0 to 6.4. The interference of other ions is the same as for Mn^{2+} .

K. SAITO

1460. **Rapid determination of gold and silver in ores [in the field].** M. Shima (*Japan Analyst*, 1953, **2** [2], 96-98).—A rapid colorimetric determination of Au and Ag in ores with the use of dithizone is proposed. A 100 to 150-g sample of well-pulverised ore is kept in a stoppered bottle with Br-ether (1 + 1) (1 to 2 ml) for 2 hr. and occasionally shaken. Water (50 ml) saturated with ether is added to the sample soln. and it is kept for a further 2 hr. to complete the extraction of Au. It is then filtered and the filtrate is evaporated, treated with aqua regia (1 to 5 ml), diluted with dil. HCl (1 + 50) (10 ml) and submitted to extraction titration with dithizone- CCl_4 standard soln. Silver is determined in the residue by dissolving it in aqua regia, diluting with dil. HNO_3 (1 + 10) and titrating with dithizone. The result is satisfactory for the estimation of Au and Ag in the field, although a little lower (up to 3 per cent. relative) than that of the ordinary assay. This defect is overcome by either modifying the extraction method according to the nature of the ore or making use of a calibration curve.

K. SAITO

1461. **Chemical analysis of beryllium. III. Determination of beryllium with hexamethylenetetramine [hexamine].** T. Akiyama (*Japan Analyst*, 1953, **2** [2], 116-117).—The separation of Al and Be with hexamine is studied. The aq. soln. immediately precipitates Al but not Be at room temp. Be is pptd. quant. if heated on a water bath for 50 min., and can be separated from a comparable amount of Al.

K. SAITO

1462. **Flame-photometric determination of strontium in sea-water.** T. J. Chow and T. G. Thompson (*Anal. Chem.*, 1955, **27** [1], 18-21).—Samples of sea-water are examined for Sr under specified conditions at $460.7 m\mu$ by the hydrogen-flame photometer. After allowance for background emission, measured at $454 m\mu$, the strontium concn. is obtained from standards that give a linear concn.-intensity relationship. The effects of band-width and radiation interferences are examined; emissions of K^+ , Mg^{2+} , Cl^- and SO_4^{2-} are negligible at $460.7 m\mu$ and that of Na^+ is eliminated in the background adjustment, but that of Ca^{2+} is significant; Cl^- , SO_4^{2-} and Mg^{2+} suppress the Sr^{2+} emission intensity slightly and Na^+ , K^+ and Ca^{2+} increase it, all proportionately to their concn. To avoid these effects, the following

procedure is recommended. Equal volumes of sea-water are added to a series of solutions of known Sr^{++} content, and from a plot of net intensities (less background) vs. concn., extrapolated to zero standard intensity, the Sr^{++} concn. of the unknown is deduced. Results of synthetic mixtures, and of sea-waters from three localities and 10 depths at each source, are presented.

D. A. PANTONY

1463. Direct titration method for the determination of barium. S. B. Deal (*Anal. Chem.*, 1955, **27** [1], 109-111).—The soln. (20 ml) containing 10 to 50 mg of Ba^{++} is diluted with isopropanol (20 ml) and the indicator [tetrahydroxyquinone (1 part) mixed with KCl (300 parts)] (0.2 g) is added. As standard 0.025 N K_2SO_4 is run in, the red colour fades, until, at the end-point, the soln. becomes orange. Ca^{++} , Ni^{++} , Cd^{++} , Cr^{+++} , Co^{++} , Mg^{++} , Mn^{++} , Zn^{++} and Hg^{++} do not interfere, but Sr^{++} leads to inconsistent and high results; Fe^{+++} , Sn^{++++} , Pb^{++} , Cu^{++} , Al^{+++} , CO_3^{--} and SO_3^{--} should be removed before titration. Results are compared with those of the BaSO_4 gravimetric method.

D. A. PANTONY

1464. The use of tetramethylthionine chloride (methylene blue) for the gravimetric determination of zinc. B. A. Platunov and E. P. Mikhailovskaya (*Uch. Zap. Leningr. Gos. Un-ta*, 1953, [169], Ser. *Khim.* N. [13], 189-202; *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 32,895).—Zinc is quantitatively pptd. by methylene blue in the presence of excess of CNS⁻, probably as $[\text{C}_{16}\text{H}_{18}\text{N}_4\text{S}_2]\text{Zn}(\text{CNS})_4$. Procedure.—To 10 ml of zinc salt soln. (containing 11 mg of Zn) add 10 ml of HCl soln. (sp. gr. 1.18) and 9 g of ammonium acetate; heat to boiling point and add 15 ml of a 1 per cent. aq. soln. of methylene blue; again heat to boiling point and ppt. with 5 ml of a 10 per cent. soln. of NH_4CNS (keeping the total vol. at 100 ml). Filter the hot soln. and wash the ppt. with hot water containing 2 ml of HCl. On ignition, the ppt. is converted into ZnO . Ca^{++} or Al^{+++} do not interfere and these ions may be determined in the filtrate. Fe^{+++} interfere.

E. HAYES

1465. Applications of the Brown and Hayes indicator systems in compleximetric titrations. H. Flaschka and W. Franschitz (*Z. anal. Chem.*, 1955, **144** [6], 421-427).—An accurate compleximetric titration of Zn is described, which makes use of a mixture of ferri- and ferro-cyanides and 3:3'-dimethylnaphthidine as a redox indicator system; the titration is performed at pH 5. Other metal ions are titratable by adding an excess of Complexone III and back-titrating with standard solutions of zinc salts, even in the presence of considerable amounts of alkaline-earth metals. Procedures for the determination of Zn, Cu, Ni, Cd, Pb, Fe, Al and total Fe plus Al are presented.

D. R. GLASSON

1466. Quantitative analysis without separation. IX. The systems Zn-Mn and Bi-Pb. N. Unohara (*J. Chem. Soc. Japan*, 1954, **75** [7], 724-726).—The thermal decomposition curves from the heating of MnSO_4 , ZnSO_4 + MnSO_4 , $\text{Bi}_2(\text{SO}_4)_3$ and $\text{Bi}_2(\text{SO}_4)_3$ + PbSO_4 are studied with a thermobalance. MnSO_4 starts to decompose before decomposition of ZnSO_4 in the mixture is complete, making the quant. analysis without separation difficult. Bi in the presence of Pb, in the form of mixed sulphates, can be determined from the weight difference on heating, provided that the amounts are of comparable order. **X. The systems Bi-Zn and Bi-Cd** (*Ibid.*, 1954, **75** [7], 726-727).

—Similar experiments were carried out with the mixtures $\text{Bi}_2(\text{SO}_4)_3$ + ZnSO_4 and $\text{Bi}_2(\text{SO}_4)_3$ + CdSO_4 . The decomposition of CdSO_4 is promoted by $\text{Bi}_2(\text{SO}_4)_3$. The analysis of Bi is unsatisfactory in mixtures with Zn or Cd.

K. SAITO

1467. Flame-photometric study of boron. J. A. Dean and C. Thompson (*Anal. Chem.*, 1955, **27** [1], 42-46).—Factors that influence the determination of boron with a Beckman DU spectrophotometer with the 9220 flame-attachment are examined, viz., the properties of boron emissions, spectrophotometer settings, solvent, pH of solvent and interference of various elements. The proposed method of analysis requires an aq. methanol solvent (1 + 1) containing < 0.5 M HCl (higher concn. depress the boron intensity) with an oxyacetylene flame under specified photometer settings. The boron is measured by the height of the emission peaks, relative to standards, allowance being made for background, taken arbitrarily as the height of the troughs between the maxima at 492, 518 and 546 m μ . Interference by many elements is claimed to be negligible in this procedure. Limits of applicability are given as 50 to 200 p.p.m. of B, and a sensitivity of 1 to 3 p.p.m. is claimed.

D. A. PANTONY

1468. Quantitative spectrographic analysis of boron. N. Ota (*Japan Analyst*, 1953, **2** [3], 205-208).—Spectrographic analysis of B (0.004 to 0.07 per cent.) in silicate, especially in marine clay, is studied by the continuous-arc method; an interrupted arc is not suitable. The sample is put in a small hole (diameter 3 mm, depth 2 mm) of a pure copper rod (diameter 6 mm) and a d.c. arc is struck (4 amp., 150 V, exposure 1 min.). Tellurium (added to the sample) is used for the internal standard and B 2497-72A compared with Te 2385-78A. The working curve is straight for 0.004 to 0.07 per cent. of B. Less than 10 per cent. of Fe in the sample does not interfere.

K. SAITO

1469. Determination of boron in coal. F. H. Kunstmann and J. F. Harris (*Brennstoff-Chem.*, 1955, **36** [1-2], 20-23).—The sample (1 g) is mixed with Na_2CO_3 (3 g) and, after ashing in a muffle furnace, the mixture is fused and then taken up in a small excess of aq. HCl. The solution is transferred to a quartz distillation flask and freed from CO_2 by refluxing while a current of air passes through. Anhydrous CaCl_2 (1 g per ml) is added to assist esterification, 20 ml of methanol are run in from a tap-funnel and the mixture is distilled in a stream of methanol vapour from a second flask containing mannitol and KOH. Sixty ml of the soln. are slowly distilled into a flask containing methanol (10 ml) and 20 per cent. aq. KOH (0.6 ml). The distillate is acidified with 0.2 N H_2SO_4 (0.3 ml in excess, bromocresol purple indicator) and freed from CO_2 , which must be excluded during the titration, then neutralised by 0.005 N NaOH (1 ml \equiv 54 μg of B) and again neutralised after addition of mannitol (2 g). A blank test is necessary. Coals from twelve South African collieries contained 0.0011 to 0.0060 per cent. of boron.

A. R. PEARSON

1470. Determination of boron in silicates after ion-exchange separation. H. Kramer (*Anal. Chem.*, 1955, **27** [1], 144-145).—A sample (> 1 g) containing 10 to 20 mg of B_2O_3 is dissolved either by (a) boiling under reflux with dil. HCl (1 + 5) (30 ml) for 20 to 25 min.; the condenser is washed and the soln. is filtered, the filtrate being made up to \approx 50 ml with water washings, or (b) fusion with a six-fold excess of Na_2CO_3 ; the cooled melt is

extracted with water (20 ml) and the soln. is made just acid with a 1-ml excess of HCl; the soln. is filtered and made up to ≈ 50 ml with water washings. To the soln. from treatment (a) or (b) is added 20 per cent. aq. NaOH until any ppt. just dissolves or until the soln. is just acid to litmus. The soln. is passed through a cation-exchange column [Amberlite IR-120 (H)], followed by four 50-ml water washings. To the eluate is added 20 per cent. aq. NaOH until the soln. is just alkaline to methyl red. After the soln. is made just acid with HCl, it is boiled (3 to 5 min.) to expel CO_2 , cooled and its pH is adjusted to 7 with 0.05 N NaOH (pH meter). Mannitol (40 g) is added and then the soln. is rapidly titrated with 0.05 N NaOH to pH 7. A blank is run similarly and, allowance having been made for it, the B_2O_3 concn. is calculated from a given conversion factor. Results for the analysis of 15 samples and synthetic mixtures are presented and compared with those from other methods. Na^+ , K^+ , Ca^{++} , Mg^{++} , Ba^{++} , Fe^{+++} , Al^{+++} , Zn^{++} and Cl^- do not interfere. Reproducibility, accuracy, ease of manipulation, blank corrections and time of operation are claimed to be good.

D. A. PANTONY

1471. Argentimetric procedure for borohydride determination. H. C. Brown and A. C. Boyd, jun. (*Anal. Chem.*, 1955, **27** [1], 156-158).—The borohydride soln. in 2 N NaOH (2 ml) is added to a mixture of 0.2 N AgNO_3 (25 ml) and 0.7 M (i.e., ≈ 4 per cent.) ethylenediamine (25 ml). After swirling, the mixture is filtered on sintered glass and the ppt. is washed with three portions of water (10 to 20 ml each). The filtrate and washings are made acid with HNO_3 (5 ml), and are titrated with standard 0.1 N NH_4CNS (Fe^{+++} indicator), nitrobenzene (20 ml) being added just before the end-point. Results are compared with those from a standard iodate method, and reasons for failure of the latter are suggested. No interference is caused by K^+ , ClO_4^- , Na^+ , formate, ethanol, acetone or cyclohexanone, but benzaldehyde leads to high results. The method is extended as a qualitative spot test for borohydride soln. D. A. PANTONY

1472. Potentiometric titration of low concentrations of boric acid anhydride in deuterium oxide and in ordinary water. L. Silverman and W. Bradshaw (*Anal. Chim. Acta*, 1955, **12** [2], 177-185).—Solutions of boron trioxide in water and in deuterium oxide are titrated potentiometrically with standard KOH soln., free from CO_2 , in the presence of mannitol. The soln. of B_2O_3 (200 ml) is first boiled under a reflux condenser for 10 min. and cooled while protected from air. Mannitol (20 g) is added and helium is bubbled through the soln. during the titration. At concn. of B_2O_3 of 50 to 150 mg per litre, the precision is < 99.5 per cent. and at a concn. of 1.1×10^{-5} M the error is ± 5 per cent. For such dil. solutions, glycerol provides a less sharply inflected titration curve when used in place of mannitol. W. C. JOHNSON

1473. The analytical chemistry of aluminium and its alloys. J. H. G. Thomson (*Chem. Age*, 1955, **72**, 225-229).—Methods of analysis of aluminium and its alloys, including the determination of trace constituents, are reviewed. N. E.

1474. Volumetric determination of aluminium with Complexone III. I. Sajó (*Magyar Kem. Foly.*, 1954, **60** [9], 268-272).—Aluminium can be determined with Complexone III with the use of indicators such as Eriochrome cyanine R, disodium hydrogen phosphate, or ferricyanide-benzidine,

provided the pH is < 6.7 . The determination can be carried out in the presence of Ca^{++} , Sr^{++} , Ba^{++} , Fe , Mn^{++} , Cu^{++} , Co^{++} , Cr^{+++} , V, Ti, SiO_4^{--} , PO_4^{--} , Cl^- , NO_3^- or SO_4^{--} without previous separation by the addition of excess of Complexone III to the soln. and back-titrating the excess with standard zinc acetate with the use of ferricyanide and benzidine as indicator. Addition of NaF liberates the Al^{+++} combined with Complexone III, which can then be determined as above. P. HAAS

1475. Rapid determination of aluminium by a volumetric method. I. Sajó (*Magyar Kém. Foly.*, 1953, **59** [10], 319-320; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 36,407).—To a solution of the sample, add a 0.05 N soln. of Complexone III, acetate buffer soln. (pH 5 to 7), 1 g of Eriochrome cyanine indicator (ground with KNO_3 , 1:500), heat and titrate with 0.05 N ZnSO_4 or CdSO_4 until the colour changes from yellow to purple-lilac. Silica interferes, as do Ca, Mn, Ti, Cl, SO_4^{--} and CO_3^{--} , when present in large amounts. E. HAYES

1476. Use of haematoxylin as an indicator for the volumetric determination of aluminium with ethylenediaminetetra-acetic acid. M. P. Taylor (*Analyst*, 1955, **80**, 153-155).—The general use of haematoxylin as a colorimetric reagent for Al suggested its use as an indicator in the titration of aluminium with ethylenediaminetetra-acetic acid (I), thus avoiding the necessity for back-titration of excess of I with other standard solutions. *Procedure*—To 10 ml of a 0.05 M soln. of I, 0.5 ml of haematoxylin indicator (prep. described) and a few drops of 40 per cent. ammonium acetate soln. are added. The aluminium soln. is run in from a burette until the liquid has a permanent pinkish-purple colour. The liquid is then buffered to pH 6 with 10 ml of ammonium acetate soln. and 2 ml of 2 M acetic acid and heated to boiling point, when the colour will revert to the original yellow. Titration is completed with the Al^{+++} soln., the temp. being maintained at $< 70^\circ \text{C}$. Ca^{++} , Mg^{++} , Ba^{++} , Sr^{++} , CO_3^{--} , SO_4^{--} , NO_3^- , Cl^- , Br^- , I^- , tartrate and acetate do not interfere; Fe and Zn react quant.; PO_4^{--} , Cu, citrate and oxalate may obscure the end-point and F⁻ bleaches the indicator. Th, Ni, Bi, Sb, Cd, Co, Pb, Hg, Mo and Sn interfere when present above certain [stated] concentrations. A. O. JONES

1477. Compleximetric titrations (chelatometry). II. Screening of aluminium, iron and manganese in titrations with murexide as indicator. R. Příbil (*Chem. Listy*, 1953, **47**, 1333-1337).—The screening of Al, Fe and Mn in compleximetric titrations of Ni and Ca with murexide as indicator has been effectively achieved by the use of triethanolamine. To determine Ni in the presence of Fe, Al and Mn, treat the soln. of these cations with 30 per cent. triethanolamine (5 to 10 ml), conc. aq. NH_3 (30 ml) and murexide, and titrate with 0.05 N Complexone III. To determine Ca in the presence of Fe, Al, Mn and Mg, treat the weakly acid soln. of salts of these metals, freed from NH_4^+ , with 30 per cent. triethanolamine (10 to 20 ml) and 0.5 N NaOH (10 ml) before titrating. G. GLASER

1478. Rapid determination of aluminium in iron and steel. Y. Kakita and Y. Yokoyama (*Japan Analyst*, 1953, **2** [2], 106-108).—The method of Kassner and Ozier for the determination of Al in iron and steel (*Brit. Abstr. C*, 1952, 44) is modified to be suitable for rapid analysis. By making use of benzene (15 ml) instead of chloroform, the extraction of aluminium oxinate is more rapid.

By changing the method of decomp. of the sample [with the use of 6 to 10 ml of dil. HNO_3 (1 + 1) and 10 ml of conc. HClO_4] and carrying out the reduction of Fe^{+++} with a saturated soln. of Na_2SO_3 (10 ml) in the presence of HNO_3 , the total time for the analysis is < 20 min. K. SAITO

1479. Rapid methods for the analysis of aluminium alloys. J. Buciewicz and Z. Doliński (*Przegl., Odlewn.*, 1953, **3** [11], 21-22; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 32,917).—A weighed sample of alloy is dissolved in NaOH soln. and metals other than Mg are separated as hydroxyquinoline complexes from a soln., at pH 7 to 7.05, containing ammonium acetate. Mg is pptd. from the filtrate with aq. NH_3 soln., the ppt. is dissolved in excess of HCl, and an excess of KBrO_3 plus KBr is added; after the addition of KI and starch, the I is back-titrated with $\text{Na}_2\text{S}_2\text{O}_3$ soln. The remaining metals are determined in separate samples by the following methods: Fe^{III} , photometrically as thiocyanate; Zn, polarographically (after treatment of the alloy with HCl or NaOH) at -1.4 V in a medium of aq. NH_3 soln. and ammonium chloride; Ni (1 to 1.5 per cent.), gravimetrically with dimethylglyoxime; Cr (up to 1 per cent.), by a volumetric method; and Ti (up to 0.3 per cent.), photometrically as the yellow compound H_4TiO_5 . E. HAYES

1480. The determination of alumina in silicates (rocks and refractories). G. W. C. Milner and J. L. Woodhead (*Anal. Chim. Acta*, 1955, **12** [2], 127-137).—Methods for the determination of Al in silicate minerals and refractories are reviewed and a new procedure is evolved. Samples (100 mg) containing > 5 per cent. of Al_2O_3 are sintered with Na_2O_2 (2 g) at 450° to 500°C , the mass is dissolved in water, the soln. is acidified with HCl and treated with SO_2 to reduce peroxy compounds of Ti, and Fe^{++} is re-oxidised with HNO_3 . Fe, Ti and Zr are removed from the soln. by shaking it with a soln. of the acid form of cupferron in CHCl_3 . The Al is then separated from SiO_4^{--} , Na^+ , Ca^{++} and Mg^{++} by pptg. it with ammonium benzoate. The benzoate ppt. is dissolved in dil. HCl and the Al is determined volumetrically with ethylenediaminetetra-acetic acid as reported earlier (*Anal. Abstr.*, 1954, **1**, 2360). Materials that contain < 5 per cent. of Al_2O_3 are first treated with H_2SO_4 and aq. HF to remove SiO_2 , which would otherwise separate from the acid soln. because a large sample (500 mg) is taken for analysis. The residue from the acid treatment is fused with KHSO_4 , the melt is extracted with dil. HCl and any Fe^{++} is oxidised with HNO_3 . The cupferron extraction and the rest of the procedure are as already described. W. C. JOHNSON

1481. The separation of the rare earths by the use of ethylenediaminetetra-acetic acid. G. Brunisholz (*Helv. Chim. Acta*, 1955, **38** [2], 455-459).—The complexes of the lanthanons (Ln) with ethylenediaminetetra-acetic acid (H_4Y) can be used for the separation of the rare earths (R). Three separation techniques are described. First, fractional separation of the free complex acids $\text{H}(\text{LnY})$ by precipitation at 80°C with $(\text{NH}_4)_2\text{Y}$ between pH 2 and 5. The process is repeated 4 to 5 times and finally the non-pptd. rare earths are reclaimed from the solution. Secondly, fractional crystallisation of the sodium salts in the presence of about 70 per cent. of uncomplexed Ln. The pH is adjusted to 4.5, NaCl (15 g in 100 ml) is added and, at room temp., the mixed crystals of cerous earths, greatly enriched in Sm and Nd, are obtained in the first fraction.

Thirdly, fractional crystallisation of the complex ammonium salts by adding to the hot soln. sufficient $(\text{NH}_4)_2\text{Y}$ to complex about 70 per cent. of the R^{+++} . The pH is adjusted to 4.5 in a volume of 100 ml and the solution is cooled. At 0°C , the crystals obtained are enriched in Nd and Sm and can be further enriched by recrystallisation from H_2O . D. G. HIGGS

1482. Radiochemical determination of cerium in fission [products]. L. E. Glendenin, K. F. Flynn, R. F. Buchanan and E. P. Steinberg (*Anal. Chem.*, 1955, **27** [1], 59-60).—Good extraction of cerium by isobutyl methyl ketone was attained in both trace and macro concn. from 8 to 10 M HNO_3 with NaBrO_3 as oxidant to convert Ce^{III} to Ce^{IV} . The Ce^{IV} was extracted into water containing H_2O_2 to reduce Ce^{IV} again to Ce^{III} when it was pptd. as oxalate for gravimetric determination of yield and measurement of radioactivity. Good separation from the large number of elements encountered in fission products is effected by this procedure as well as a considerable saving in time and effort over the ceric iodate method. D. A. PANTONY

1483. Studies of gallic acid complexes with metals and their analytical applications. I. Spectrophotometric investigation. C. Venkateswarlu, M. S. Das and V. T. Athavale (*Proc. Indian Acad. Sci., A*, 1954, **40** [6], 260-269).—A systematic spectrophotometric investigation is described of the reaction of solutions containing Ti with gallic acid, with particular reference to the effects of pH, gallic acid concn. and ageing. Interference by most metals, with the exception of Fe, Mo and V, can be suppressed by the addition of ammonium tartrate and adjustment of the pH to 5.2. Phosphate interferes by producing a ppt., and oxalate and citrate reduce the intensity of the colour of the complex. Beer's law is obeyed at all the wavelengths investigated. The method is recommended for the estimation of TiO_2 in concn. ranging from 0.01 to 10.0 mg per 100 ml, as the sensitivity is high and the colour is stable for 24 hr. A. JOBLING

1484. Polarography of indium. M. Bulovová (*Chem. Listy*, 1954, **48** [5], 655-662).—A study of the reduction of In^{+++} on the dropping-mercury electrode has shown that the character of the polarographic curve of indium is influenced by the anion of the indifferent electrolyte, by surface-active substances and by temperature. Deformable anions (I^- , Br^- , Cl^- , CNS^- , acetates, oxalates) greatly activate the deposition of indium. In the presence of non-deformable anions (ClO_4^- , ClO_3^- , NO_3^- , SO_4^{--} , F^-), the current is controlled by the rate of a preceding electrode reaction. The effect of adsorbents depends on the composition of the excess of electrolyte. Gelatin, added in small amounts, supports the reversibility of the electrolytic process. To determine indium in the presence of cadmium, their E_1 being identical, the recommended polarographic medium is an acetate buffer of pH 4.7; a wave is obtained which represents the sum of the indium and cadmium concentrations. By adding subsequently a few crystals of NaF, KF or NH_4F , a wave corresponding to the concn. of Cd only is obtained. The difference between the two wave heights gives the concn. of indium. G. GLASER

1485. Studies in photo-electric colorimetry. VI. A new colour reaction of thallium with p-phenetidine and its application to photo-electric colorimetry. S. Iijima and Y. Kamemoto (*J. Chem. Soc. Japan*,

Pure Chem. Sect., 1954, **75** [12], 1294-1297).—Tervalent thallium oxidises *p*-phenetidine in a weakly acidic soln. (pH 3.0 to 3.7) to a quinonoid form and gives a stable intense purple colour (limit of identification of Tl is 0.14 μg per 0.04 ml). The absorption spectrum has max. at 305 m μ and 540 m μ . The extinction coeff. is proportional to the concn. of Tl down to $< 2.0 \times 10^{-4} M$, so this reaction can be used for the colorimetric determination of Tl. Substances such as Au^{III} , Fe^{III} and Pb^{IV} , which have redox potentials $> +0.36 V$, give a similar coloration and disturb both the detection and the determination of Tl. K. SAITO

1486. Quantitative analysis of germanium. I. Spectrographic determination of germanium in ores by the intermittent-arc method. H. Goto and Y. Yokoyama (*J. Chem. Soc. Japan, Pure Chem. Sect.*), 1954, **75** [12], 1305-1308).—Small amounts of Ge (0.005 to 0.08 per cent.) in ores can be determined satisfactorily as follows. The sample (10 g) is treated with HNO_3 (≈ 70 ml) and transferred to a Scherrer flask (*J. Res. Nat. Bur. Stand.*, 1936, **16**, 253). Sufficient HCl and H_2O are added to produce 100 ml of 6 N HCl soln. and the GeCl_4 is distilled with a current of CO_2 into an ice-cooled adapter, containing 5 ml of H_2O , until 10 ml of distillate are collected (15 min.). This is neutralised with 3.4 N NaOH and made up to 100 ml together with 10 ml of CuCl_2 soln. (30 mg per ml). The soln. (0.1 ml) is put on a carbon electrode (diameter 5.5 mm, length 25 mm) and an intermittent arc is struck (d.c. 120 V, 7 amp.; interruption factor 1 to 4, period 0.7 sec.; exposure 120 sec.). The intensity of Ge 2651-Å is compared with that of Cu 2618-Å. The amount of NaCl in the final soln. should be kept approx. constant for a reproducible result to be obtained. Arsenic, which distils from 6 N HCl soln. with Ge, does not interfere with the result unless the amount is > 0.2 per cent. in the final soln. K. SAITO

1487. A rapid colorimetric analysis of germanium and titanium by use of paper chromatography. N. Matsuura (*Japan Analyst.*, 1953, **2** [2], 135-17).—One drop (5 μl) of germanium soln. (1 to 10 μg per μl) is developed on filter-paper with butanol (saturated with 2 N HCl) to form a spot (R_F , 0.30). After being dried under an infra-red lamp, it is developed with haematoxylin and placed in the optical path of a photometer (without drying) for the extinction to be measured. By comparing with spots of the standard soln., the amount of Ge is estimated with an accuracy of ± 10 per cent. No interference is caused by As (R_F , 0.66), Sb (0.66), Sn (0.67), Bi (0.63) and Fe^{III} (0.10). Titanium (1 to 7 μg per μl) can be estimated similarly by developing with tannic acid-acetic acid reagent. K. SAITO

1488. Anion-exchange separation of tin, antimony and tellurium. G. W. Smith and S. A. Reynolds (*Anal. Chim. Acta*, 1955, **12** [2], 151-153).—Tracer quantities of $^{119}\text{Sn}^{\text{IV}}$, $^{124}\text{Sb}^{\text{IV}}$ and $^{125}\text{Te}^{\text{IV}}$ are separated in a column of Dowex-1 anion-exchange resin. Elution is effected with 0.1 M oxalic acid followed by $M \text{ H}_2\text{SO}_4$. W. C. JOHNSON

1489. Adsorption of lead and bismuth by glass. T. Schönfeld and S. Neumann (*Monatsh.*, 1954, **85** [4], 921-935).—The surfaces of various glasses can be differentiated by determining the amount of adsorption and desorption of radioactive Pb^{II} . The adsorption is measured by determining the amount of radioactive Pb in a solution of known strength of radioactive lead nitrate, before and after the glass has been immersed in the solution

for some hr. The difference between the two determinations gives the amount of Pb^{II} adsorbed. The Pb^{II} is pptd. as PbCrO_4 and measured in a Geiger counter. Details of the method and underlying theory are given. The method yields information about the chemical and thermal pre-history of samples of glass of identical composition. The adsorption of Bi is also studied. P. HAAS

1490. Application of infra-red spectroscopy to the determination of impurities in titanium tetrachloride. R. B. Johannesen, C. L. Gordon, J. E. Stewart and R. Gilchrist (*J. Res. Nat. Bur. Stand.*, 1954, **53** [4], 197-200).—Infra-red absorption spectroscopy is used to determine impurities in TiCl_4 . Procedure—A 50-mm conical glass cell, with sodium chloride windows that are sealed on with plasticised cellulose nitrate, is used from 2 to 9.5 μ , and a 0.25-mm cell, with Teflon spacer, between 9.5 and 15 μ . Methods are described for filling and sealing the cells, without admission of moisture, by distillation or suction. Wavelengths in μ and limits of detection in p.p.m. for various impurities in commercial TiCl_4 are as follows: HCl, 3.53, 2; VOCl_3 , 4.84, 40; COCl_2 , 5.51, ≈ 2 ; chloroacetyl chloride, 5.55, 0.5; SiCl_4 , 8.14, 200; hydrolysis products, 8.45, (—). VOCl_3 can also be detected at 1 p.p.m. at 390 m μ , and SiCl_4 at high sensitivity by emission spectroscopy. The fundamental vibrations calculated for pure TiCl_4 (99-9991 per cent.) agree with those obtained previously from the Raman spectrum. A. B. DENSHAM

1491. Separation of titanium, tungsten, molybdenum and niobium by anion exchange. J. L. Hague, E. D. Brown and H. A. Bright (*J. Res. Nat. Bur. Stand.*, 1954, **53** [4], 261-262).—The elution characteristics of Ti, W, Mo and Nb, in solution in aq. HCl-HF mixtures of different composition, from the anion-exchange resin Dowex-1, are investigated in a polystyrene column with polystyrene receivers; quantitative separations are possible. Further work is in progress on detailed procedures for the separation and determination of components of mixtures of commercial interest. A. B. DENSHAM

1492. Compleximetric determination of zirconium. A. Musil and M. Theis (*Z. anal. Chem.*, 1955, **144** [6], 427-430).—A direct volumetric determination of Zr by Complexone III is presented. Standard and test solutions are titrated in approx. N HCl, with the use of Chromazurol S (Geigy) as indicator. The end-point may be determined either directly or on back-titration with the Complexone. Fe does not interfere. The test solutions (0.01 to 0.1 M to Zr) are boiled beforehand to ensure that all Zr is present as ZrO^{II} . D. R. GLASSON

1493. Semi-micro method for determination of cyanate ion in presence of interfering substances. W. H. R. Shaw and J. J. Bordeaux (*Anal. Chem.*, 1955, **27** [1], 136-138).—The mixture containing cyanate ion is passed through a cation exchanger (Dowex 50); the eluate is collected and acidified, the CNO^- being rapidly converted to NH_4^+ . The column is eluted with NaOH soln. and rinsed, thus leaving only Na^+ . The acidified eluate is passed through the column, the NH_4^+ being quant. retained and all other ions rinsed from the columns and discarded. NH_4^+ are eluted and determined by treatment with Nessler's reagent and measurement of the absorbance. The standard deviation of a batch of ten duplicate analyses of a soln. containing 170 micromoles per litre was ± 1.5 per cent. G. P. COOK

1494. Diphenylcarbazone as an internal indicator in volumetric analysis. I. Determination of ferrocyanide by lead nitrate. G. S. Deshmukh (*Bull. Chem. Soc. Japan*, 1954, **27** [9], 623-624).—A simple and direct determination of ferrocyanide by standard lead nitrate with diphenylcarbazone as internal indicator is described. The accuracy compares favourably with that of other classical procedures. Solutions of $K_4Fe(CN)_6$ at concn. $>0.03 N$ may be used; the pink or red colour developed by Pb^{2+} with diphenylcarbazone is immediately destroyed by the $K_4Fe(CN)_6$. D. R. GLASSON

1495. Colorimetric determination of phosphorus. L. Erdey, V. Fleps and E. Bodor (*Acta Chim. Hung.*, 1954, **5** [1-2], 65-80).—A colorimetric estimation of P is investigated in which the molybdophosphate complex is reduced with ascorbic acid. From a study of the influence of various factors, the following procedure is recommended. Ten ml of a stock solution of phosphate (containing ≈ 1 to $10 \mu g$ per ml) are pipetted into a 50-ml calibrated flask, acidified with 20 ml of $N H_2SO_4$, and then 5 ml of 2 per cent. ammonium molybdate soln. and 10 ml of 0.1 N ascorbic acid soln. are added. The soln. is made up to the 50-ml mark and allowed to stand for 15 min., when the light absorption is measured photometrically, using an S 72 filter. The method is successfully applied to the determination of P_2O_5 in alumina. A 0.5-g sample is fused with 2.5 g of a (1 + 1) Na_2CO_3 -borax mixture in a platinum crucible. The melt is dissolved in 30 ml of H_2O and 13.5 ml of 4 N H_2SO_4 with careful warming, and the crucible is washed out. After adding a further 25 ml of 4 N H_2SO_4 , the soln. is made up to 100 ml and used as a stock soln.; 20 ml of this are taken for the phosphorus determination, which is carried out as above, but without the addition of more H_2SO_4 . For larger amounts of P, a 10-ml aliquot is used, with the addition of 10 ml of $N H_2SO_4$. Concn. down to $0.05 \mu g$ per ml of P_2O_5 can be estimated. The results show good reproducibility, the error being <0.005 per cent. of P_2O_5 for a content of 0.01 to 0.02 per cent., and less for higher contents of P_2O_5 . J. H. WATON

1496. Determination of the phosphorus pentoxide content of silicate rocks. V. Fleps, B. Simó and L. Erdey (*Acta Chim. Hung.*, 1954, **5** [1-2], 81-89).—The previously described colorimetric method (*Anal. Abstr.*, 1955, **2**, 1495) for the determination of phosphorus, in which ascorbic acid reduces the molybdophosphate complex, is applied to the estimation of P_2O_5 in silicate rocks. A micro-, as well as a macro-, method is given, both of which give results in good agreement with parallel gravimetric estimations. The results given by the colorimetric and gravimetric methods differ by <5 per cent. The colorimetric technique is the more rapid, requiring only 30 min. apart from the solution of the sample. J. H. WATON

1497. General volumetric method for phosphorus pentoxide in phosphoric acid and alkali and alkaline-earth phosphates. R. Navarro (*Afinidad*, 1954, **31**, 421-430).—Procedures based on double or triple titrations with phenolphthalein and methyl orange are given for the determination of alkali, alkaline-earth and ammonium phosphates in the presence of H_3PO_4 , free bases, Na_2CO_3 , H_3PO_4 - H_2SO_4 , or H_3PO_4 -HCl. The alkaline-earth ions are precipitated as oxalates and the ammonia is removed by boiling with alkali, the phosphates being finally titrated in the form of alkali phosphates.

L. A. O'NEILL

1498. Titrimetric determination of phosphate ions with standard solution of magnesium sulphate. E. Bakács (*Magyar Kem. Foly.*, 1954, **60** [8], 229-231).—A description is given of a volumetric method for the determination of PO_4^{3-} with standard $MgSO_4$, and Mg^{2+} with standard KH_2PO_4 . In aq. alcohol soln., the ppt. formed is crystalline. Eriochrome black T is used as indicator, the pH being adjusted to 10 by ammonium chloride-aq. NH_3 soln. buffer. P. HAAS

1499. Permanent colour standards for determination of phosphate by molybdenum blue method. E. P. Parry and A. L. McClelland (*Anal. Chem.*, 1955, **27** [1], 140-141).—Standards are prepared by mixing various proportions of 0.883 per cent. Cu^{2+} (as $CuSO_4$) and 0.01 per cent. bromophenol blue soln. at pH 4.53 (Na acetate-acetic acid buffer soln.). Spectra of these soln. and those of molybdenum blue are compared, and stability data are presented. D. A. PANTONY

1500. Coulometric determination of orthophosphate. W. N. Carson, jun., and H. S. Gile (*Anal. Chem.*, 1955, **27** [1], 122-123).—A soln. containing 0.005 to 0.05 millimole of PO_4^{3-} and 1 to 2 N in mineral acid is pipetted on to cation-exchange resin (1 ml) just covered with CO_2 -free H_2O in a 3-ml sintered-glass funnel. The filtrate and washings are mixed with 50 per cent. KBr (500 μl) and the strong acids are neutralised with 0.1 N NaOH (methyl red). The soln. is made just acid with 0.01 N HCl or HNO_3 , to an excess of 10 to 25 μl . Exact neutrality is attained by coulometric titration with a platinum cathode-silver anode (methyl red). The titration is continued coulometrically with thymol blue as indicator; end-point colours are matched with standards prepared from buffer soln. Precision is given as ± 0.005 to $0.016 M$ over the range of concn. examined. UO_2^{2+} , SO_4^{2-} and NO_3^- do not interfere, but weak acids must be removed before titration. D. A. PANTONY

1501. Determination of small quantities of arsenic. I. S. P. Bystrov and N. V. Egorov (*Aptekhnoc Delo*, 1954, **3** [6], 12-16).—In the determination of small quantities of arsenic (2 to $10 \mu g$) by the Sanger-Black method (reduction with Zn and dil. H_2SO_4 in the presence of $SnCl_2$ and reaction of the AsH_3 evolved with mercuric bromide paper), identical results are obtained when H_2SO_4 is replaced by HCl. Without $SnCl_2$, the method is less sensitive and the results less reproducible. Standard solutions containing 2 to $10 \mu g$ of As per ml (prepared by dissolving As_2O_3 in NaOH soln., diluting with water and adjusting to pH 5 to 6 with HCl) can be stored in glass vessels for at least 15 days without loss of As; after storage for 30 days, the As content of the soln. falls to 30 per cent. of the initial. E. HAYES

1502. Nephelometric determination of arsenic in copper and zinc. P. V. Marchenko (*Ukr. Khim. Zh.*, 1954, **20** [1], 77-82).—To 1 ml of a solution containing 30 to 200 μg of As are added 1 ml of $10^{-4} M$ $HgCl_2$, 5 ml of 20 per cent. aq. $SnCl_2$ and conc. HCl to 8 N. The solution is heated at $100^\circ C$ for 15 to 20 min. for 30 to 100 μg of As, or 10 min. for 150 to 200 μg of As, and the turbidity is measured in a photocolormeter. The results agree with those given by Evans' original method (*Analyst*, 1929, **54**, 524), in which hypophosphite is used for reduction.

R. TRUSCOE

1503. Determination of arsenic in coal. L. J. Edgcombe and H. K. Gold (*Analyst*, 1955, **80**, 155-157).—The air-dried ground coal (1 g), mixed with MgO and moistened with lime water, is completely ashed at 675° C. The residue is treated with 5 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 g of hydrazine sulphate, 0.02 g of KBr, 10 ml of conc. HCl and 10 ml of water and is distilled into 2 ml of conc. HNO_3 and 10 ml of water; the distillation is repeated twice, after addition of more HCl and water. The distillate is evaporated to dryness, moistened, re-evaporated and then washed with 2.5 ml of water into a calibrated tube of special design, which contains 2 ml of 0.01 N I and 2 ml of N NaHCO_3 soln. The liquid is then treated slowly with 2 ml of a H_2SO_4 - Na_2MoO_4 soln. (prep. described), transferred to a beaker and treated with aq. sodium metabisulphite soln. until the iodine colour is just discharged. The thoroughly mixed liquid is treated with 1 ml of a dil. SnCl_2 soln. and diluted with water to 10 ml in the calibrated tube. The absorption of the liquid is then measured in a Spekker absorptiometer with an Ilford No. 608 filter. A blank determination is made similarly without the coal. The calibration graph is prepared in the same way with known amounts of a standard As_2O_3 soln. The relation is linear up to 100 μg of As_2O_3 . A. O. JONES

1504. Spectrophotometric determination of bismuth with sodium diethyldithiocarbamate. K. L. Cheng, R. H. Bray and S. W. Melsted (*Anal. Chem.*, 1955, **27** [1], 24-26).—A sample containing up to 0.3 mg of Bi^{+++} is dissolved in hot HNO_3 or HCl and HNO_3 , and the soln. is treated with a complexing mixture [1.5 M aq. NH_3 containing 5 per cent. v/v of disodium ethylenediaminetetra-acetate and 5 per cent. w/v of NaCN] (10 ml), 0.2 per cent. aq. diethyldithiocarbamate (1 ml) and CCl_4 (10 ml). After shaking (30 sec.), the organic layer is separated, filtered and its absorption is measured at 370 or 400 μ . Standards are treated similarly, and from the linear relationship between their absorption and concn. the Bi^{+++} concn. is deduced. Hg^{++} and Pb^{++} interfere at 370 μ but not at 400 μ ; the test is more sensitive at the former wavelength. There is no interference from Cd^{++} , Cu^{++} , Ag^+ , NO_3^- , SO_4^{--} , Cl^- , acetate, ClO_4^- , PO_4^{--} , tartrate or citrate. Results for the analysis of a standard lead-based alloy are given, and a detailed procedure for the determination of Bi^{+++} in the alloy is described.

D. A. PANTONY

1505. Studies on the determination of organic compounds of metals by the extraction method. IX. Extraction and colorimetric estimation of bismuth and antimony with phenazone and potassium iodide. E. Sudo (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [12], 1291-1294).—Antimony can be extracted from a 2 to 5 N H_2SO_4 soln. (≈ 20 ml) containing 5 per cent. aq. phenazone soln. (3 ml) and 10 per cent. KI soln. (2 ml) with CHCl_3 (5 ml). The extinction coeff. of the chloroform layer at 430 to 460 μ is proportional to the concn. of Sb (1 to 100 μg) and can be utilised for its determination. The max. absorption (365 μ) cannot be used because of the intense absorption of the blank soln. The amount of reagents, the acid concn. and other conditions are examined. Several common ions, including Cu, Fe, Al and Ca, interfere with the result, but Hg, Sn^{++} and As^{+++} do not. Bi can be extracted with CHCl_3 or isopentanol in a similar way from a less acidic soln. (0.5 to 1.5 N H_2SO_4) and the solvent layer has max. absorption at 500 and 345 μ , the extinction of the former being proportional to the

bismuth concn. (1 to 50 μg). Errors are caused by Cu, Fe and As^{+++} , but not by As^{+} , Zn, Co, Ni or Cr.

K. SAITO

1506. Polarographic study of vanadium. K. Micka and A. Tockstein (*Chem. Listy*, 1954, **48** [5], 648-654).—The polarographic behaviour of V^{IV} and V^{V} salts in $\text{Na}_2\text{B}_4\text{O}_7$, Na_2CO_3 , Britton-Robinson buffer, acetate buffer and H_2SO_4 has been studied. The effects of adding Complexone III are discussed and the polarographic curves are described.

G. GLASER

1507. Indirect colorimetric analysis of vanadium. N. Oi (*J. Chem. Soc. Japan*, 1954, **75** [8], 841-843).—Ephraim's method for the detection of V with FeCl_3 and dimethylglyoxime (*Helv. Chim. Acta*, 1931, **14**, 1266) is applied to its colorimetric determination. V^{V} is reduced to V^{IV} by boiling in < 6 N HCl. FeCl_3 is added and the amount of Fe^{++} produced on reduction by V^{IV} is determined colorimetrically with dimethylglyoxime in ammoniacal soln. in the presence of tartrate. The extinction coeff. at 530 μ is proportional to the V content (50 to 500 μg in 30 ml). The colour is unstable and the extinction must be measured within 10 min. after the addition of the reagents. An excessive amount of Fe^{+++} should be avoided. Interference is caused by Cu (> 25 μg), Mn (> 50 μg) and Cr (> 500 μg).

K. SAITO

1508. Separation of quadrivalent vanadium from quinquevalent vanadium. I. Tsubaki and S. Hara (*Japan Analyst*, 1953, **2** [2], 91-92).—Various methods for the separation of V^{IV} from V^{V} are compared. The pptn. of V^{IV} with phosphate at pH 7 is not satisfactory, because the ppt. is contaminated by V^{V} . The pptn. of V^{V} with oxine in an acetate buffer soln. (pH 5.5 to 6.0) is recommended.

K. SAITO

1509. Reversible polarographic reduction of niobium. [Preliminary communication.] D. J. Ferrett and G. W. C. Milner (*Nature*, 1955, **175**, 477).—Polarography of a solution of Nb in 0.1 M disodium ethylenediaminetetra-acetate at pH 3-0.5 gives waves with half-wave potential -0.609 V and -10.5 V (S.C.E.). The latter wave coalesces with the hydrogen wave but the former is shown to be reversible at pH 3.2 and to be proportional to the concn. of Nb over a range of 500 to 5 μg per ml. The sensitivity can be increased by square-wave polarography.

E. J. H. BIRCH

1510. Separation of protoactinium and niobium by liquid-liquid extraction. F. L. Moore (*Anal. Chem.*, 1955, **27** [1], 70-72).—Conditions for the separation of Nb from Pa by organic liquid extraction are examined by a radio-counting technique. Results are presented for attempted separations by extraction of Nb and Pa into either xylene, chloroform, diisopropylcarbinol or, especially, diisobutylcarbinol from either HCl, HNO_3 , H_2SO_4 , oxalic acid, H_2SO_4 -HCl, HCl- H_2SO_4 -oxalic acid, or HF- H_2SO_4 soln. In the most successful separation, Nb is extracted by diisobutylcarbinol from a 6 M HF-6 M H_2SO_4 soln.; the Nb is readily re-extracted with water.

D. A. PANTONY

1511. Improvements in methods for determination of sulphur in combustible solids. I. Reduction of the time necessary for incineration of Eschka mixture. L. Rodriguez Pire and J. A. Corrales Zarauza (*Inst. Nac. Carbón, Bol. Inform.*, 1954, **3** [18], 13-21).—The Eschka method for the determination of S in combustible solids is the most

suitable in industry, because of its simple execution, rapidity, economy of material, reagents and labour, and the possibility of making simultaneous determinations. Variations in the method to prevent loss of S during incineration, including the use of Br water, oven-preheating at various temperatures and duration of the heating, were examined, as was the possibility of performing six assays simultaneously. The method developed is to introduce the coal - Eschka reagent mixture into the oven previously heated to 600° C, increasing the temperature by 20° C per min. to 800° C, maintaining an oxygen-rich atmosphere in the oven by passing in O₂ at a rate sufficient to change the oven atmosphere every 3 min., and starting a few min. before the introduction of the sample. Under these conditions, the incineration is complete in 30 min.; good results are given for the extreme case of a hygroscopic lignite with a high sulphur content (10.6 per cent.).

D. LEIGHTON

1512. Spectrophotometric determination of traces of selenium with [3:3'-]diaminobenzidine. J. Hoste and J. Gillis (*Anal. Chim. Acta*, 1955, **12** [2], 158-161).—3:3'-Diaminobenzidine yields with SeO₃²⁻ an intense-yellow piasezenol (bis-2:1:3-benzoselenadiazole) (Hoste, *Brit. Abstr. C*, 1951, 328) with an absorption max. at 348 mμ ($\epsilon = 10,200$). The reaction is applied to the photometric determination of Se. The sample soln. (25 ml) is mixed with 25 ml of a 0.1 per cent. soln. of 3:3'-diaminobenzidine tetrahydrochloride in dil. HCl to provide a final HCl concn. of 0.1 N. The colour intensity reaches a max. in 50 min., and is measured at 348 mμ in a 1-cm Corex cell. Five μg of Se gives an extinction of ≈ 0.45 , and the Beer-Lambert law holds for 0.25 to 2.5 μg of Se per ml. At high concn. ($E > 0.69$) pptn. occurs. The colour is stable for 3 hr. Most common colourless ions do not interfere. Fe⁺⁺⁺ is masked with NH₄F and Cu⁺⁺ with ammonium oxalate; SO₃²⁻ gives a colourless ppt. but SO₄²⁻ and TeO₃²⁻ do not interfere.

W. C. JOHNSON

1513. Ultra-violet spectrophotometry of tellurium sols. R. A. Johnson and B. R. Andersen (*Anal. Chem.*, 1955, **27** [1], 120-122).—Red sols of Te are prepared by treating a soln. of 0.1 to 0.7 mg of Te^{IV} in dil. HCl (1 to 8 milli-equivalents) with 4 per cent. aq. gum acacia soln. (3 ml). The soln. is diluted to 35 ml and, when boiling, 3 M H₃PO₃ (5 ml) is run in rapidly. The sol is digested for 15 min. and then cooled for 15 min.; after adjustment of the vol. to 50 ml, the absorption is measured at 240 to 290 mμ, and compared with standards at the selected wavelength. The u.v. spectral properties of the red, amber, purple and blue sols are described. Although the visible spectra differ, the absorption max. in the range 280 to 290 mμ and obedience to Beer's law are common to all types. Standard error is given as ± 0.15 p.p.m. of Te. By careful selection of the wavelength of absorption measurement, interferences due to Sn⁺⁺⁺⁺, Fe⁺⁺⁺, Bi⁺⁺⁺, VO₃³⁻, Mo⁺⁺⁺⁺, Ti⁺⁺⁺, Cu⁺⁺, Pb⁺⁺, Hg⁺⁺, Tl⁺, Cr⁺⁺⁺, Ni⁺⁺, Zn⁺⁺ and Al⁺⁺⁺ can be avoided. Strong oxidising agents and complex-forming compounds interfere seriously.

D. A. PANTONY

1514. Source of error in determination of chromic oxide using perchloric-sulphuric acid digestion method. K. M. Day (*Science*, 1954, **120**, 717-718).—In the method of Bolin *et al.* (*Science*, 1952, **116**, 634) it is concluded that temp., time and acidity are critical factors during the digestion period. Loss of Cr appears to occur by the production of H₂O₂

as a decomposition product, as a result of high temp. and concn. by prolonged digestion. In estimating Cr in dried cow manure, it was found that, when a 400 to 500-mg sample was digested at a temp. such that a clear orange-coloured digest was obtained in 10 or 12 min., results showed a standard deviation of ± 0.02 per cent. in the range 0.3 to 0.5 per cent. of Cr₂O₃.

H. F. W. KIRKPATRICK

1515. Studies on the reactions of chromic-complex compounds with ion-exchange resins. I. Y. Inoue, A. Kawamura, K. Wada and H. Okamura (*Japan Analyst*, 1953, **2** [1], 21-26).—The exchange reaction between an anion-exchange resin (Amberlite IR-4B) and oxalatochromic complex salts is studied in order to utilise this reaction for the analysis of chrome tanning liquor. For the exchange reaction to proceed smoothly the resin must be treated with acetic acid (5 per cent.) before the chromic-complex soln. is passed through. Neither K trioxalatochromate nor K dioxalatochromate is exchanged satisfactorily by an anion-exchange resin which has other acid radicles like Cl⁻, SO₄²⁻, C₂O₄²⁻, etc. The break through of the complex salt from the resin column is characteristic of the anion radicle of the resin and is independent of the co-existing ions in the original soln.

K. SAITO

1516. Studies on the reactions of chromic-complex compounds with ion-exchange resins. II. The reaction between oxalatochromate and the anion-exchange resin Amberlite IR-4B. Y. Inoue, A. Kawamura, K. Wada and H. Okamura (*Japan Analyst*, 1953, **2** [2], 121-125).—The influence of temp., concn. of the complex soln. and the preliminary thermal treatment of the resin on the exchange of K dioxalatochromate and K trioxalatochromate with Amberlite IR-4B is studied. The previous finding (see Abstract 1515 above), that the acetate form of the resin is the most desirable for the exchange to take place smoothly, is confirmed under different conditions. The higher the temp. of the soln. to be flowed, the smaller is the break through of Cr from the column. Resin in chloride or sulphate form is not satisfactory at low temp., but exchanges well with the anionic complex at 50° C.

K. SAITO

1517. Separation of molybdenum and tungsten by sublimation in a hydrogen chloride atmosphere. A. Aaremae and G. Assarsson (*Z. anal. Chem.*, 1955, **144** [6], 412-415).—The process for separating Mo and W by sublimation of the trioxides in an atmosphere of hydrogen chloride (Spitzin, *Z. anal. Chem.*, 1928, **75**, 433) is unsuitable for analytical purposes, since the MoO₃ tends to form Mo₂O₃Cl₆ of low volatility, while the WO₃ volatilises significantly at $> 220^\circ \text{C}$.

D. R. GLASSON

1518. Compound of molybdates with alizarin S. T. N. Nazarchuk (*Ukr. Khim. Zh.*, 1954, **20** [4], 417-423).—Alizarin S and H₂MoO₄ give a coloured complex, stable at pH 2 to 5, of the composition [alizarin]₂[H₂MoO₄]. The complex is stable at dilutions of 10⁻⁴ to 10⁻³ M and is not decomposed by fluorides, which decolorise Al and Fe complexes. The solutions are decolorised by oxalates, citrates and tartrates. The coloration can be used for the colorimetric determination of Mo.

R. TRUSCOE

1519. Rapid photometric determination of molybdenum in steel. K. Protiva (*Chem. Listy*, 1954, **48** [5], 779-780).—A rapid method for the colorimetric determination of Mo in a variety of steels, based on the formation of a red complex of Mo with KCNS

in the presence of HNO_3 and SnCl_2 , is described. **Procedure**—Dissolve the sample (1 g) containing up to 0.5 per cent. of Mo in a hot acid mixture [dil. HNO_3 (1 + 1) containing ≈ 5 per cent. of dil. H_2SO_4 (1 + 3)] (20 ml). Boil the soln. to expel nitrogen oxides, dilute with water (20 ml), heat to boiling point and oxidise with 1.5 per cent. KMnO_4 (15 ml). After 1 min., decompose the excess of KMnO_4 with FeSO_4 soln. (10 to 15 ml) [prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (200 g) in water, acidifying with conc. H_2SO_4 (25 ml) and diluting to 1 litre]. Neutralise the clear soln. with 4 N NaOH , pour it into hot 4 N NaOH (120 ml), cool and dilute to 500 ml. To a 20-ml aliquot, add in the following order, dil. HNO_3 (1 + 1) (10 ml), 10 per cent. KCNS (10 ml) and SnCl_2 soln. (10 ml) [prepared by diluting a soln. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (30 g) in conc. HCl (150 ml) with dil. HCl (1 + 3) (1 litre)]. Compare the red-brown coloration with a standard. Modified procedures for vanadium steels, high-speed steels and steels of high molybdenum content are given. G. GLASER

1520. Spectrophotometric determination of uranium with morin. M. T. Beck and E. Hantos (*Magyar Kem. Foly.*, 1954, **60** [8], 244-247).—The uranyl ion forms a stable complex with morin at pH 4 to 7, the ratio of UO_2^{2+} to morin being 1 to 2. The properties of this compound make a precise spectrophotometric and colorimetric determination of U possible. P. HAAS

1521. Spectrochemical analysis of fluorine by use of the band spectrum of calcium fluoride. III. Studies on the fluorine contained in sediments and soils at Tamagawa Hot Springs in Akita Prefecture. K. Fuwa (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [12], 1257-1259).—Sediment, soil and rock samples were submitted to spectrophotometric analysis for the fluorine contents to be measured. The dry sample (when wet, dry at 110°C) is mixed well with the same amount of CaCO_3 and put on a carbon electrode. A d.c. arc is passed and the band head in the CaF_2 molecular spectrum at 5291 Å is observed through a spectroscope of the constant-deviation type. Its persistence in the cathode flame of the arc is measured (*J. Chem. Soc. Japan*, 1951, **72**, 985). The result is discussed from geochemical aspects. K. SAITO

1522. Detection of volatile fluorides in air. R. Mavrodineanu (*Contr. Boyce Thompson Inst.*, 1954, **18** [1], 82-84).—Fagan's method (Marconi's Wireless Telegraph Co., Ltd., and Christopher P. Fagan, Brit. Pat. 566,389, Date Appl. 28.12.44) is modified. Dry sampling is used with a strip of blotting paper impregnated with a suitable reagent [thorium nitrate (1.75 g per litre) and 0.1 per cent. sodium alizarin-sulphonate], which reacts with HF and other volatile fluorides readily convertible into HF, e.g., SiF_4 and H_2SiF_6 . The degree of bleaching is a function of the concn. of the gas and the duration of exposure. R. H. HURST

1523. Determination of chloride by automatic titration. H. B. Jones and H. Baum (*Anal. Chem.*, 1955, **27** [1], 99-100).—A procedure is described for the application of the Beckman automatic titrator Model K to the determination of Cl^- in organic compounds by the AgNO_3 titration following Na_2O_2 fusion. D. A. PANTONY

1524. Titrimetric estimation of the chloride ion by use of eosin as indicator. J. Bognár and J. Vereskői (*Acta Chim. Hung.*, 1954, **5** [1-2], 105-109).

—Eosin may be used as an adsorption indicator in the argentimetric estimation of Cl^- , if the soln. contains acetic acid $> 0.2\text{N}$ and if 50 per cent. of alcohol or acetone is added. The optimum chloride ion concn. is 0.01 N. Dilution of the Cl^- soln. with other organic liquids has a favourable effect on the position of the colour change of the eosin, but only for dioxan is the change sufficiently sharp. With dioxan, the titration can be performed in neutral or acid medium, provided that the pH > 2 . The presence of other electrolytes does not affect the titration. J. H. WATON

1525. Permanganate method for the determination of iodine in iodised salt. A. S. Schvets (*Apteknoe Delo*, 1954, **3** [6], 35-36).—Potassium iodide (≈ 0.001 per cent.) in iodised table salt is oxidised to KIO_3 with alkaline KMnO_4 and the iodate is determined iodimetrically. **Procedure**—To 100 ml of a 20 per cent. soln. of iodised salt, add 4 ml of 0.1 N KOH and an excess (2 ml) of 0.1 N KMnO_4 soln.; add 1 ml of 0.1 N HCl or H_2SO_4 and 2 ml of 0.1 N oxalic acid soln. and heat gently to destroy the excess of KMnO_4 . To the cooled soln., add 0.2 g of KI , set aside for 3 min. in the dark, and titrate with 0.005 N $\text{Na}_2\text{S}_2\text{O}_3$, using starch as indicator. The mean error is ± 2.8 per cent. E. HAYES

1526. Determination of iodine in common salt by the catalytic reduction of ceric ions. M. Dubravčić (*Analyst*, 1955, **80**, 146-153).—The influence of NaCl on the catalytic reduction of $\text{Ce}(\text{SO}_4)_2$ was studied so that the method previously published (Rogina *et al.*, *Anal. Abstr.*, 1954, **1**, 87) could be used for the determination of I in common salt. The effects of Ca, Mg, Fe^{++} , Br and some other constituents present in common salt were also examined. In the method developed, the reagents and apparatus are as previously described with the addition of a standard soln. of I-free salt (prep. described). The salt (10 g) is dissolved in ≈ 50 ml of water, the solution is filtered and the filtrate is diluted to 100 ml. In each test-tube are placed 6 ml of water, 2 ml of salt soln., 0.5 ml of As_2O_3 soln. and 0.5 ml. of H_2SO_4 and the tubes are placed in a water bath at 30°C . Addition of the cerium salt and the subsequent manipulations are as previously described (*loc. cit.*). Two to four tubes in every set of twenty tubes must contain reference standards of KI soln. (0.1 μg per ml) and these are used, if necessary, to correct the calibration graph. With iodised table salt, the vol. of soln. used depends upon the iodine content of the salt and, as the concn. of NaCl in the tubes will be low, the requisite amount of a standard soln. of I-free NaCl must be added to bring the NaCl content to 0.2 g. In this high-range procedure, as many as eight tubes may be used, two to four tubes containing reference standards with the same vol. of reagents as before, but a more conc. soln. of KI (1 μg per ml) is necessary. The presence of NaCl in the reaction mixture permits the determination of $< 0.01 \mu\text{g}$ of I in 10 ml of the mixture. A. O. JONES

1527. Determination of the iodide ion in presence of the bromide ion. L. Szekeres (*Magyar Kem. Foly.*, 1954, **60** [6], 165-168).—To the soln. containing iodide and bromide ions, chlorine water and excess of NaHCO_3 are added, resulting in the formation of NaIO_3 , NaOBr and NaOCl ; the two last compounds are reduced with urea, sodium formate, or alcohol, which leaves the iodate ion to be determined iodimetrically. The accuracy of the method is not affected by the presence of large amounts of Cl^- or Br^- . P. HAAS

1528. Contribution to the polarographic determination of manganese and iron. M. Hemala and Z. Valčíková (*Chem. Listy*, 1954, **48** [5], 777-778).—The interfering effects of Mg and Ca on the polarographic determination of Mn and Fe in water in triethanolamine soln. have been investigated. Small amounts of Mg lower the wave of Mn and at higher concn. of Mg the wave disappears altogether. The effect of Mg on the polarographic determination of Fe is similar, but less pronounced. Calcium in low concn. does not affect the determination of Mn, but irregularly lowers the wave of Fe. For the polarographic determination of Mn in water, it is advisable to separate Mn from Mg by pptg. it with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ from aq. NH_3 soln. in the presence of ammonium salts. G. GLASER

1529. Paper chromatography of inorganic ions. X. A study of rhenium, technetium and some other non-metals. M. Lederer (*Anal. Chim. Acta*, 1955, **12** [2], 146-150).—The following separations are investigated, $^{186}\text{ReO}_4^-$ and $^{99}\text{TcO}_4^-$, $^{32}\text{PO}_4^{3-}$ and $^{35}\text{SO}_4^{2-}$, $^{186}\text{ReO}_4^-$ and MoO_4^{2-} , $^{99}\text{TcO}_4^-$ and MoO_4^{2-} , SeO_4^{2-} and TeO_4^{2-} . Butanol shaken with N HCl, 1.5 N HNO_3 or 1.5 N aq. NH_3 is used as eluent. W. C. JOHNSON

1530. Determination of iron in the presence of large amounts of phosphate by titration with disodium dihydrogen ethylenediaminetetra-acetate. L. T. Butt and N. Strafford (*Anal. Chim. Acta*, 1955, **12** [2], 124-126).—Ferric iron (30 mg) can be determined in the presence of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (1 g) by titrating with disodium ethylenediaminetetra-acetate (I), the pH being adjusted to 2.0 to 2.4 and NH_4CNS being used as indicator. *Procedure*—To the acid soln. (25 ml) containing 3 to 30 mg of Fe, add 0.2 g of ammonium persulphate followed by 3 M aq. NH_3 to the production of a faint permanent turbidity. Transfer to a 100-ml separating funnel, add 1 ml of 20 per cent. aq. NH_4CNS and 20 ml of pentanol. Titrate with 0.05 M I in 1-ml, and later in 0.5-ml, portions until the alcoholic layer is colourless after shaking. Separate the aq. layer and adjust it to pH 2.3 with 3 M aq. NH_3 . Return the soln. to the funnel and titrate with 0.05 M iron alum until the pentanol is faintly pink after shaking [1 ml of 0.05 M I — ml of 0.05 M iron alum] $\times 2.8$ = mg of iron]. W. C. JOHNSON

1531. Determination of iron and titanium in the presence of fluoride. (Application of a de-masking action in volumetric analysis.) S. Suzuki, K. Harimaya and M. Ueno (*J. Chem. Soc. Japan*, 1954, **75** [8], 838-841).—The reduction of Fe^{3+} by zinc amalgam is retarded by the presence of F⁻ so that the time required is nearly doubled (> 60 sec. for Fe < 100 mg). This masking action is broken down by the addition of Be^{2+} , which forms a more stable complex with F⁻. Fe^{3+} can be titrated with either $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 standard solution without being affected by Be^{2+} . The time for the reduction of Ti^{4+} to Ti^{3+} (≈ 45 sec. for up to 100 mg of Ti) by zinc amalgam is not prolonged by F⁻ but the oxidation of Ti^{3+} appears to be retarded. It is therefore recommended to add Be^{2+} to the titanium soln. after the reduction to the trivalent state by zinc amalgam. Precise experimental conditions and results are given. K. SAITO

1532. Tests on the filter-photometric determination of iron by nitrilotriacetic acid. W. Nielsch and G. Böltz (*Z. anal. Chem.*, 1955, **144** [6], 401-406).—Ferric compounds form deep-yellow complexes with

nitrilotriacetic acid, which are determined photometrically by using mercury radiation of 316 m μ . Extinction coefficients for the iron complex are nearly constant over the pH range 4.50 to 7.70, and the colour is independent of the type of acid present. Weaker complexing agents, e.g., tartaric acid and other buffer mixtures including ammonium salts, can be used for adjusting the pH without affecting the extinction. The influence of temp. and excess of reagent are investigated. The nitrilotriacetic acid derivative is stable up to pH 10 and is almost as stable as its ethylenediaminetetra-acetic acid analogue. The use of a filter-photometer is preferable for the latter, whereas a spectrophotometer can be used in the u.v. range for the former. D. R. GLASSON

1533. Rapid analysis by use of ion-exchange resins. II. Rapid determination of iron in the presence of aluminium. S. Kojima and H. Kakihana (*Japan Analyst*, 1953, **2** [2], 133-134).—The mixed soln. of Fe^{3+} and Al^{3+} (both 1 to 10 milli-equiv.) is passed through the cation-exchange resin Amberlite IR-120 (H), and the column is eluted with KI soln. (2 per cent. in 0.5 N HCl) (300 ml). Iodine (equiv. in amount to the Fe^{3+}) is obtained in the eluate, which is titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$ soln. by the usual method. Al^{3+} and Fe^{3+} can be eluted from the column subsequently. K. SAITO

1534. Simultaneous spectrophotometric determination of [ferrous] iron and total iron with 1:10-phenanthroline. A. E. Harvey, jun., J. A. Smart and E. S. Amis (*Anal. Chem.*, 1955, **27** [1], 26-29).—The sample (0.3 g) is dissolved in dilute H_2SO_4 and the soln. is made up to 250 ml. An aliquot (1 ml) is treated with 0.3 per cent. 1:10-phenanthroline soln. (10 ml) and 0.2 M potassium hydrogen phthalate soln. (5 ml) and made up to 25 ml. The absorption is measured at 396 m μ (total Fe) and 512 m μ (approx. Fe^{2+}) and the values are converted to concn. from a calibration curve. By difference, the approx. Fe^{3+} concn. is obtained, and its deduced (slight) absorption at 512 m μ is deducted from the measured value at 512 m μ to give the corrected accurate Fe^{2+} concn. The effects of 24 extraneous cations and 14 anions are listed and of these the reducing ions and anions that readily form complexes with Fe^{2+} interfere. Results of the analysis of 5 prepared samples are given. Average precision is given as 1.5 per cent. for total Fe and 2.3 per cent. for Fe^{2+} . D. A. PANTONY

1535. Determination of ferrous iron in basic slags containing sulphide and ferric iron. S. Hirano and D. Ishii (*Japan Analyst*, 1953, **2** [3], 214-218).—The determination of Fe^{2+} in basic slags or iron ores is so largely affected by sulphide S and Fe^{3+} that the result is always too high (up to 7 times too great when the contents of Fe^{2+} are low). The use of Hg^{2+} and H_3PO_4 prevents the reduction of Fe^{3+} by H_2S , which is produced during the decomp. of the sample. *Procedure*—The sample (≈ 100 mesh, 0.5 to 1.0 g) is taken in a dry stoppered flask and air is expelled by passing in CO_2 . Saturated HgCl_2 soln. (≈ 7 per cent., 15 ml for up to 0.5 per cent. of sulphide S) is added and the sample is decomposed with H_2PO_4 (1 + 1) (30 to 50 ml) and cooled. These procedures must be carried out in an atmosphere of CO_2 . The residue is dissolved in 6 N H_2SO_4 (50 ml) and water (100 ml), filtered quickly and washed with 2 N H_2SO_4 . The filtrate and washings are united and titrated with 0.1 N KMnO_4 . Vanadate ion appears to be reduced to vanadyl ion

in all these procedures. For samples containing Mo and W the method should be modified. The whole procedure takes ≈ 30 min. K. SAITO

1536. Steric hindrance in analytical chemistry. III. 1:2'-Pyridylisoquinoline and the ferroin reaction. H. Irving and A. Hampton (*J. Chem. Soc.*, 1955, 430-432).—1:2'-Pyridylisoquinoline is synthesised by the cyclisation of 2-phenyl-N-picolinoylethylamine with PCl_5 - AlCl_3 to 3:4-dihydro-1:2'-pyridylisoquinoline and the dehydrogenation of this with palladium black. 1:2'-Pyridylisoquinoline in a buffer at pH 5 to 6 with hydroxylamine and traces of Fe^{II} gives a stable reddish blue colour (absorption max. at 585 $\text{m}\mu$, $\epsilon = 11,500$); it also gives a brown cuprous complex. It is suggested that the failure of diisoquinolyl to give the reaction must be due to steric effects. The 3:4-dihydro derivative also gives a Fe^{II} complex (absorption max. at 586 $\text{m}\mu$, $\epsilon = 15,600$), a pale-yellow colour with Fe^{III} and a brown colour with Cu^I . Beer's law is obeyed for up to 25 p.p.m. of Fe . E. J. H. BIRCH

1537. Mass-spectrometric analysis of gas contained in iron and steel. E. Kato (*Japan Analyst*, 1953, 2 [2], 98-101).—A small-scale mass-spectrometer (radius of the magnetic field, 12 cm) is used for the analysis of gases in metals. The gas is collected by fusing the sample *in vacuo*, it is then passed into a reservoir by a mercury pump and submitted to analysis by the usual method. Some examples of the analysis of soft steel and stainless steel are shown. The influence of the gas flow through the gas leak of the mass spectrometer is studied and an effort is made to minimise the error by fluctuations in the flow and in ionisation efficiency. K. SAITO

1538. Determination of nickel, manganese, cobalt and iron in high-temperature alloys, using anion-exchange separations. J. L. Hague, E. E. Maczkowske and H. A. Bright (*J. Res. Nat. Bur. Stand.*, 1954, 53 [6], 353-359).—In the detailed procedure described, 1 g of the alloy is dissolved in a (1 + 3, by vol.) mixture of conc. HNO_3 and conc. HCl , and the Nb, Ta, W and Si are rendered insoluble by four successive dehydrations with HCl . From the resulting HCl soln. Mo and Cu are pptd. with H_2S and removed along with the dehydrated oxides. The filtrate is evaporated several times with HCl (1 + 1) and H_2O_2 (30 per cent.) to produce a soln. of the chlorides in their proper valence. This soln. is transferred to an ion-exchange column (12 in. \times 1 in., Dowex-1, 200 to 400 mesh) and the Ni, Mn, Cr and some other elements are collected in the first fraction by elution with 9 N HCl ; Co is collected in a second fraction by elution with 4 N HCl , and Fe in a third by elution with N HCl . Mn and Ni are then determined in aliquots of the first fraction by the persulphate-arsenite titration and dimethylglyoxime gravimetric methods, respectively. The Co is determined by electrolysis from a slightly ammoniacal chloride solution containing hydroxylamine hydrochloride, and the Fe by reduction with SnCl_2 and titration with $\text{K}_2\text{Cr}_2\text{O}_7$. A complete analysis takes several days as ≈ 3 hr. are required for each of the ion-exchange fractionations. The accuracy and reproducibility of the results are generally satisfactory, although values for Co are ≈ 0.5 to 0.8 mg too high, and (owing to unfavourable diffusion in the column) those for Fe tend to be ≈ 0.5 per cent. too low. W. J. BAKER

1539. Paper chromatography of cobalt (III), copper (II) and nickel (II) acetylacetonates. E. W.

Berg and J. E. Strassner (*Anal. Chem.*, 1955, 27 [1], 127-129).—A soln. (60 ml) containing 2 per cent. of each of Co^{+++} , Cu^{++} and Ni^{++} is treated with 3 per cent. H_2O_2 (20 ml) and, after digestion (15 min.), the pH is adjusted to 7 with sodium acetate. Acetylacetone-ethanol mixture (1 + 1) (20 ml) is added, the mixture is warmed and the acetylacetonates are extracted with methyl isopropyl ketone-*n*-butanol mixture (1 + 1) (50 ml). After several hr., the organic layer becomes green and it is then separated. The organic layer is spotted on No. 1 Whatman paper 2.5 in. wide and, when dry, the spots are subjected to upward-flow chromatography in methanol-cyclohexane-dioxan solvent (6:84:10, by vol.). R_F values are given as Co^{+++} , 0.64; Cu^{++} , 0.27; Ni^{++} , 0.00. Figures for the solubilities of the complexes in organic solvents and the dielectric constants of the soln. are given.

D. A. PANTONY

1540. Determination of metals with a standard solution of potassium ferrocyanide. VI. Determination of cobalt salts. E. Fujita (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, 75 [12], 1235-1238).—The experimental conditions for the titration of Co^{++} with $\text{K}_4\text{Fe}(\text{CN})_6$ standard soln. (0.05 M) are studied. This titration can be used only for the determination of 2 to 6 mg of Co, free from cations that form ppt. with $\text{Fe}(\text{CN})_6^{4-}$, and from ions that undergo redox reactions with it. Iodine-starch soln. is used as indicator. The pH value of the cobalt soln. must be 6.0 to 6.4, and the titration carried out slowly (5 to 10 sec. per drop).

K. SAITO

1541. Determination of traces of metals by extraction of inorganic compounds with organic solvents. I. Micro-determination of cobalt. S. Ikeda (*Japan Analyst*, 1953, 2 [3], 218-222).—The extraction of the Co-CNS complex from its aq. soln. at pH 1 to 4.5 is studied with various solvents. The absorption curve of Co-CNS in org. solvents shows two max. at 620 and 320 $\text{m}\mu$. A mixed solvent of *n*-butanol and ethyl acetate (1 + 5) gives the biggest extinction coeff. for both bands, which are in accord with Beer's law (for 10 to 50 μg of Co). No interference results from the presence of Ni (< 1 mg), Pb (< 1 mg), Cr (< 1 mg), Mn (< 1 mg), Fe (< 0.5 mg), Cu (< 30 μg at 620 $\text{m}\mu$, < 150 μg at 320 $\text{m}\mu$) and Bi (< 20 μg at 620 $\text{m}\mu$, < 100 μg at 320 $\text{m}\mu$).

K. SAITO

1542. Compleximetric titrations (chelometry). VII. Catechol violet as a new specific indicator; determination of nickel, cobalt, manganese, zinc, magnesium and cadmium. M. Malát, V. Suk and A. Jeničková (*Chem. Listy*, 1954, 48 [5], 663-668).—In alkaline media, catechol violet (catecholsulphonaphthalein) forms with a number of bivalent cations intensely coloured complexes that are weaker than those formed with Complexone III. This property allows direct compleximetric determination of Ni, Co, Mn, Zn, Mg and Cd. *Procedure*.—Treat the soln. of the metal, in a max. concn. of x mg per 100 ml of soln., with y volumes of a buffer soln. A or B [(1 + 1) and (1 + 5) mixtures, respectively, of N NH_4Cl and N NH_3 soln.], and with 3 to 5 drops of a 0.1 per cent. aq. soln. of the indicator. Titrate with a standard soln. of Complexone III of suitable concn. (0.1, 0.01, 0.002 M), until the colour changes from green-blue (blue for Zn) to red-violet. The x and y values for the metals are: Ni, 30, 0.1 of A; Co, 5 to 6, 0.1 of A; 10 to 12, 0.2 of A; Mn, 25, 0.1 of A (add a little NH_4OH to the neutral soln.

before adding the buffer); Zn, 20, 0.1 of A; 40, 0.2 of B; Mg, 20, 0.1 of B; Cd, 40, 0.1 of B.

G. GLASER

1543. Polarographic determination of high nickel and cobalt content in alloys. K. Protiva (*Chem. Listy*, 1954, **48** [5], 778-779).—A polarographic procedure, which is more rapid than older methods, for the determination of high Ni and Co content in steel and special alloys is described. *Procedure*—Dissolve the sample (0.1 g) in boiling dil. HNO_3 (1 + 1) (5 ml) and dil. HCl (1 + 1) (5 ml), evaporate to dryness, ignite the residue, add conc. HCl (5 ml) and hydrazine sulphate (0.25 g) and evaporate again to dryness. Dissolve the residue, after igniting it, in dil. HCl (1 + 1) (3 ml), dilute the soln. to 50 ml, and add pyridine (5 ml) to ppt. Fe, Cr, Ti, etc. Add NH_4Cl (3 g) and 1 per cent. gelatin solution (5 ml), dilute to 100 ml and polarograph in the presence of air. Simultaneously, analyse a standard sample of similar composition; from the height of the Ni and Co wave in the standard, the content of these metals in the sample can be derived. For a Ni and Co content of 10 to 13 per cent., the accuracy of the method is ± 0.30 per cent. One determination takes 45 to 50 min. G. GLASER

1544. The thermogravimetry of analytical precipitates. LXIV. Determination of rhodium. C. Duval, P. Champ and P. Fauconnier (*Anal. Chim. Acta*, 1955, **12** [2], 138-141).—Metallic rhodium in grains < 1 mm in diameter undergoes surface oxidation when heated in air at temp. > 662° C, but the metal obtained by the pyrolysis of the complexes with thionalide, 2-mercaptobenzoxazole and thiobarbituric acid is resistant to oxidation up to $\approx 1000^\circ\text{C}$. The complexes can be dried and weighed on the thermobalance without decomposition between the following temp.: (thionalide) 79° to 205° C, (2-mercaptobenzoxazole) 92° to 150° C, or they can be heated at about 417° C or 459° C, respectively, and weighed as Rh. The complex with thiobarbituric acid can be decomposed and the Rh weighed above 480° C. W. C. JOHNSON

1545. Chemical analysis of a soda-lime - magnesia - silica glass described as standard glass No. 1. Chem. Analysis Committee Society Glass Tech. (*J. Soc. Glass Tech.*, 1954, **38**, 54-62).—Complete details are given of the procedure and results for the determination of SiO_2 (fusion with Na_2CO_3 and final treatment with HF), Al_2O_3 [as $\text{Al}(\text{OH})_3$], CaO (as oxalate), MgO (as phosphate), Na_2O (as zinc uranyl acetate), K_2O (as cobaltinitrite), S (oxidation and separation as BaSO_4), total Fe_2O_3 (colorimetric, thioglycollic acid), and TiO_2 (colorimetric, H_2O_2). J. A. SUGDEN

1546. Detection of certain ions in 10-10 to 10-15-gram particles. B. K. Seely (*Anal. Chem.*, 1955, **27** [1], 93-95).—Modified spot-test techniques, applicable to 10-10 to 10-15-g quantities, are described for the detection of Cu^{++} , Co^{++} , Ni^{++} , Fe^{++} , Na^+ , K^+ , I^- and CO_3^{--} , especially in atmospheric dusts. Essentially, the technique involves the microscopical inspection of a gelatin - glycerol medium sensitised with a Hg^2 salt and treated with a specific reagent for the sub-micro quantity of the ion under examination. D. A. PANTONY

1547. The five per cent. salt-spray test and its acetic acid modification. W. D. McMaster (*Bull. A.S.T.M.*, 1955, [No. 203], 62-69).—The limitations and practical value of the A.S.T.M. 5 per cent. salt-spray test (B117-49T) for assessing the quality and

film-thickness of paints and rust-proof or metallic coatings are discussed. The method is unsuitable for testing most electroplated parts, and more accurate results are rapidly obtained by the addition of 1 per cent. of glacial acetic acid to the 5 per cent. salt solution, which is used at 95° F. The acetic acid modification is suitable for all salt-spray testing and not only for testing Cd, Zn and Cr coatings on steel or die-castings and for anodised or phosphated Al and its alloys. New car-parts lasted 450 to 2300 hr. in salt-spray before pinhole corrosion occurred, but only for 16 to 48 hr. in the acetic acid solution, the failures being identical in every stage with those observed on parts taken from cars in service. W. J. BAKER

See also Abstracts 1553, 1560.

3.—ORGANIC ANALYSIS

1548. Determination of carbon-14 in solutions of ^{14}C -labelled materials by means of a proportional counter. A. Schwebel, H. S. Isbell and J. D. Moyer (*J. Res. Nat. Bur. Stand.*, 1954, **53** [4], 221-224).—A simple precise method for the assay of ^{14}C -labelled substances is described. *Procedure*—One ml of a solution of the substance is placed in a stainless-steel open cell at the bottom of a gas-flow counter. The β -particles from the ^{14}C ionise the stream of quenching gas flowing through the counter, leading to momentary discharges between a high-voltage anode and the walls of the counter. The solvent used must have a low v.p., its vapour must not form a conducting path and it must not creep. Formamide is recommended for carbohydrates, glycol for alkaline substances and, with a sequestering agent, for alkaline-earth carbonates; dimethyl-formamide and 90 per cent. H_2PO_4 are also useful. Counting efficiency is accurately proportional to 1/d of the solution. Calibration requires a solution of known activity. A. B. DENSHAM

1549. Determination of carbon and fluorine in highly fluorinated materials. H. E. Freier, B. W. Nippoldt, P. B. Olson and D. G. Weiblen (*Anal. Chem.*, 1955, **27** [1], 146-149).—The method is a modification of Clark's method (*Brit. Abstr. C*, 1951, 450). Modifications include the following: (a) a simultaneous carbon determination has been incorporated in the procedure, (b) the temp. has been raised from 900° to $\approx 1100^\circ\text{C}$, (c) the Grote absorber has been slightly modified, (d) the acid-base titration has been altered and (e) a small amount of moisture has been introduced into the combustion tube. The relative error of carbon and fluorine determination was < 1.0 per cent. in the nineteen compounds tested. Reproducibility from ten analyses of 2:2:3:3:4:4:4-heptafluorobutyl acrylate was ± 0.05 per cent. on a mean carbon content of 33.1 per cent. and ± 0.16 on a mean fluorine content of 52.3 per cent. Metal ions which retain fluorine at the operating temp. give low fluorine results. G. P. COOK

1550. Use of mixed adsorbents in chromatographic separation of organic compounds. J. K. Carlton and W. C. Bradbury (*Anal. Chem.*, 1955, **27** [1], 67-70).—A number of organic compounds representing several different classes were adsorbed on binary mixtures of commonly used adsorbents. The results obtained show that, with mixed adsorbents generally, (a) adsorption is characteristic of one component of the mixture, the other serving as a diluent, or (b) adsorption is shared between the two adsorbents

and varies almost linearly with percentage composition of the mixture. In (a) there is little or no deviation from the R_F values exhibited by the adsorbate on the stronger of the two adsorbents. With mixtures of B_2O_3 and silicic acid, an unusual interaction takes place which results in an adsorption strength that is higher than that of either of the pure components and selective towards amines.

G. P. COOK

1551. Halogen-cobaltous acetate-acetic acid solutions in organic qualitative analysis. P. C. Daidone (*Anal. Chem.*, 1955, **27** [1], 103-104).—The colours formed when active unsaturated compounds are treated with freshly prepared halogen-cobaltous acetate-acetic acid solution are listed.

G. P. COOK

1552. Purity of *n*-butane, isobutane, isobutene and *n*-octane from freezing points. N. C. Krouskop, G. Pilcher and A. J. Streiff (*Anal. Chem.*, 1955, **27** [1], 107-108).—Measurements were made on the lowering of the freezing points of *n*-butane, isobutane, isobutene and *n*-octane on the addition of known amounts of probable impurities. The results covering the range 100 to 92 mole per cent. of the major component show that these systems follow the ideal-solution laws in this respect.

G. P. COOK

1553. K-Capture spectroscopy. Iron-55 X-ray absorption determination of sulphur in hydrocarbons. H. K. Hughes and J. W. Wilczewski (*Anal. Chem.*, 1954, **26** [12], 1889-1893).—X-rays from the radioactive source (^{55}Fe) are passed through the liquid sample in a small cell. The extent to which the X-rays are absorbed is dependent on the quantity of S present. The transmittance is measured with a Geiger counter and scaler, and the sulphur content is calculated on the observed absorbance, the density of the sample and the known or approximated C to H ratio of the sample. The method is applicable for the determination of S in the range 0.05 to 2.7 per cent. Elements other than C, H and S must not be present in amounts > 0.01 per cent. The standard deviation is ± 0.026 per cent. of S.

G. P. COOK

1554. An accurate method of analysis for small quantities of ethylene. A. Shepp and K. O. Kutschke (*Canad. J. Chem.*, 1954, **32** [12], 1112-1115).—The method (≈ 0.5 per cent. accurate for samples containing as little as 0.03 ml of ethylene in mixtures with ≈ 1.5 ml of ethane) involves hydrogenation over a Ni-kieselguhr catalyst. The catalyst chamber is a small glass bulb (≈ 4 ml) maintained at $100^\circ \pm 2^\circ C$. A known vol. of gas is mixed with a known vol. of H, and the mixture is passed over the catalyst until the vol. is constant. The diminution in vol. is taken as the vol. of ethylene present. A reaction time of about 5 hr. is required for 0.04 to 0.10 ml of ethylene in about 0.12 ml of gas mixture with 0.12 to 0.16 ml of H.

R. J. COLE

1555. The analysis of combustion products. IV. The polarographic determination of the lower organic peroxides. H. Brischweiler and G. J. Minkoff (*Anal. Chim. Acta*, 1955, **12** [2], 186-200).—The half-wave potentials of some lower alkyl and acyl hydroperoxides and dialkyl peroxides have been determined; they become less negative on passing from H_2O_2 up the series. The limiting diffusion currents have been shown to be proportional to the concn. of individual peroxides and

to be additive in mixtures. Alkyl hydroperoxides differing by two carbon atoms can be distinguished by the different positions of their waves. H_2O_2 yields an anodic wave in alkaline soln. and can therefore be determined in the presence of the organic peroxides which yield no such wave. H_2O_2 can also be separated by adding La acetate, when $La(OH)_2OOH$ is pptd. The effect of aldehydes on the polarographic determination of peroxides has also been investigated.

W. C. JOHNSON

1556. X-ray diffraction identification of alcohols by their xanthate derivatives. G. G. Warren and F. W. Matthews (*Anal. Chem.*, 1954, **26** [12], 1985-1987).—Potassium xanthate derivatives of twenty four of the commoner alcohols were prepared and their X-ray powder patterns were determined. Homologously related structures were noted when patterns such as those of normal primary C_4 , C_5 and C_6 alcohol derivatives were compared or those of the C_{10} to C_{18} compounds. A similarity is also noted among the C_3 , C_4 and C_5 primary iso-compounds.

G. P. COOK

1557. Ethanediol. British Standards Institution (B.S. 2537:1955, 9 pp.).—Ethanediol must be miscible with H_2O in all proportions, and a (1 + 1) mixture must not deposit any solid matter at $-30^\circ C$. The specific gravity and distillation range are prescribed, and limits are given for ash, acidity, chlorine and sulphate content, with methods for their determination.

H. P. PAGE

1558. Analysis for industry. [Determination of aldehydes and ketones.] J. P. G. Farr (*Ind. Chem.*, 1955, **31**, 36-37; 90-92).—Methods for determining aldehydes and ketones are reviewed. The uses of NH_3 , amino compounds, semicarbazide, substituted hydrazines, hydroxylamine and HCN are mentioned. (150 references.)

D. R. PECK

1559. Determination of high-molecular-weight ketones. L. D. Metcalfe and A. A. Schmitz (*Anal. Chem.*, 1955, **27** [1], 138-139).—The basis of the method is the hydroxylamine hydrochloride (I) reaction with ketones. The I in a mixed solvent of 65 per cent. of isopropanol and 35 per cent. of methanol is treated with the sample, a measured excess of organic base (octadecenylamine) (II) being added to facilitate complete reaction by combining with the liberated HCl. At the end of the reaction period, unchanged amine is titrated with standard HCl in isopropanol to a bromophenol-blue endpoint. A titration is carried out on a blank containing the same quantities of I and II as with the sample. The difference between the blank and the sample gives a direct measure of the carbonyl-group content of the sample. Application of the method to purified ketones and ketone-fatty acid mixtures gave good results. The procedure has also been successfully applied to some aldehydes of high mol. weight.

G. P. COOK

1560. Determination of organic soda [equivalent] in aluminate solutions by an ion-exchange method. H. Shehyn (*Anal. Chem.*, 1955, **27** [1], 61-62).—The aluminate soln. (50 ml) is made up to 500 ml. An aliquot (25 ml) of the solution is then diluted with hot water (50 ml). At $80^\circ C$, CO_2 is passed in to ppt. the Al^{+++} , together with F^- and PO_4^{3-} , and the ppt. is separated on a paper previously washed with 2 N NaOH. The filtrate (I) and water washings are evaporated to 30 to 40 ml, and a similar filtrate (II) is obtained from a CO_2 pptn. of the ppt. after solution in NaOH. I is passed slowly through a

cation-exchange column (Amberlite IR-120), which is finally washed with water (200 ml). The eluate, free from MoO_4^{2-} and VO_3^- , is boiled for 5 min. under reflux, cooled and titrated with 0.1 N NaOH (phenolphthalein). II is treated similarly and the sum of the two titrations minus a blank of 0.4 ml represents the soda equiv. of all acids present in the original aluminate soln. After titration, the eluate is diluted to 250 ml with water and aliquots (100 ml each) are taken for SO_4^{2-} (Ba^{++} pptn.) and Cl^- (Ag^+ pptn.) determinations that are carried out by standard gravimetric methods. With the use of given equations, the difference of the soda equiv. of total acids and that of H_2SO_4 plus HCl gives the equiv. of organic acids. Results are given for aluminate soln.; reproducibility is claimed to be satisfactory.

D. A. PANTONY

1561. Chromatography of carboxylic acids on a silica gel column with a benzene-ether solvent system. D. S. Kinnory, Y. Takeda and D. M. Greenberg (*J. Biol. Chem.*, 1955, **212** [1], 379-383).—A column-chromatographic method is described for the separation of organic acids in which 0.05 N H_2SO_4 on silica gel is used as the stationary phase and benzene-ether as the solvent system. The method separates citric, α -oxoglutaric, succinic, fumaric, malic, acetic, propionic, butyric, pyruvic, α -oxopyruvic, α -oxovaleric and lactic acids. The recoveries are 80 to 100 per cent.; most are > 90 per cent. The solvent paper used prevents esterification of the acids and gives sharp peaks on the elution curve. The sensitivity of the method permits detection of 2 micro-equivalents of each acid. The acid fractions are located with methyl red, and are titrated with 0.001 N NaOH with phenol red as indicator.

J. N. ASHLEY

1562. The determination of dissociation constants of dibasic acids. H. Irving, H. S. Rossotti and G. Harris (*Analyst*, 1955, **80**, 83-94).—Existing methods for determining the Brønsted dissociation constants $^{\text{a}}K_1$ and $^{\text{a}}K_2$ of dibasic acids are discussed critically. The variation of optical density with pH for polybasic acids is discussed mathematically and, by a new treatment of the function derived for dibasic acids, a method is developed in which the co-ordinates of the maxima (or minima) and points of inflexion in the experimentally determined graph of absorbancy against pH are used for solutions containing the same total concn. of reagent. Applications of the method to the determination of the dissociation constants of the sparingly soluble reagents 5-nitroso-oxine, 8-hydroxyquinazoline, 8-hydroxy-2:4-dimethylquinazoline and 5-hydroxy-quinoxaline are described. It is shown that values of dissociation constants may also be obtained from the dependence on pH of other physical properties of the system.

A. O. JONES

1563. Reaction of deoxy sugars with anthrone. L. H. Koehler (*Anal. Chem.*, 1954, **26** [12], 1914-1916).—Red colours, with anthrone-sulphuric acid, were given by 2-deoxy-D-glucose, 2-deoxy-D-ribose and 2-deoxy-D-xylose, in contrast to the blue-green colours exhibited by fully hydroxylated sugars. Deoxypentoses showed greatest absorbance at 550 and 560 μ and deoxyglucose at 520 μ . By using different heating times and concn., characteristic reaction rates and colour intensities were obtained.

G. P. COOK

1564. Identification of organic compounds. VIII. Micro-identification of alkyl halides, O-alkyl and N-alkyl groups by paper chromatography. M.

Večeřa and J. Gasparič (*Coll. Czech. Chem. Commun.*, 1954, **19**, 1175-1178).—A method is described for the conversion of alkyl halides into the corresponding thiuronium salts and the identification of these by paper chromatography, the spots being developed with bromocresol green. Substances containing O- and N-alkyl groups can be converted into the corresponding alkyl halides, and then treated similarly. In contrast to previous methods, this requires only 1 to 3 mg of sample, and enables mixed ethers and mixtures of alkyl halides to be identified. Isomeric alkyl groups cannot be distinguished in this way. [This is a translation into English of a paper that was published originally in *Chem. Listy*, 1954, **48**, 1360.]

M. KAPEL

1565. Determination of hydroxymethyl groups in 1:2-glycols and related substances. J. C. Speck, jun., and A. A. Forist (*Anal. Chem.*, 1954, **26** [12], 1942-1944).—The method is based on the oxidation of hydroxymethyl groups by IO_4^- , with measurement of the formaldehyde produced after reducing IO_3^- and excess of IO_4^- with SO_2^{--} . The formaldehyde is determined by the formation of the coloured formaldehyde-chromotropic acid dye and measurement of the absorbance at 570 μ . The precision in the analysis of thirty-eight glucose samples was $< \pm 1.1$ per cent. and results were good with a variety of polyhydroxy compounds. Maltose gives high values.

G. P. COOK

1566. Determination of methylhydrazine. H. McKennis, jun., and A. S. Yard (*Anal. Chem.*, 1954, **26** [12], 1960-1963).—A study of the reaction of methylhydrazine with *p*-dimethylaminobenzaldehyde in aq. H_2SO_4 is presented. The compound formed is highly coloured and the reaction forms the basis of a micro-method for the determination of methylhydrazine; a wavelength of 458 μ is the most suitable for spectrophotometric measurement. Some amines interfere with the determination as well as hydrazine itself. The oxidation of methylhydrazine by acidic IO_3^- follows the stoichiometry of hydrazine oxidation and forms the basis for the determination of larger quantities of methylhydrazine.

G. P. COOK

1567. Detection of beta-hydroxyethylamines by pyrolysis with sodium chloroacetate. M. J. Rosen (*Anal. Chem.*, 1955, **27** [1], 114-116).—Pyrolysis of β -hydroxyethylamines with sodium chloroacetate gives acetaldehyde as the decomposition product. The acetaldehyde is detected by the blue colour it gives when absorbed by a soln. of sodium nitroprusside containing diethanolamine. The colour reactions of forty-four amines and nitrogen-containing surface-active agents after pyrolysis with sodium chloroacetate are listed.

G. P. COOK

1568. Polarographic investigation of the cysteine-cysteine system. II. The polarography of cystine. M. Kalousek, O. Grubner and A. Tockstein (*Coll. Czech. Chem. Commun.*, 1954, **19**, 1111-1122).—In view of the anomalous behaviour of cysteine and cystine in various potentiometric and colorimetric procedures, as well as the discrepancies in the values quoted for the oxidation potential of the cysteine-cysteine system, this system was investigated polarographically. The system is an irreversible one, so that its apparent oxidation potential has no real significance. [This is a translation into Russian of a paper that was published originally in *Chem. Listy*, 1953, **47**, 1143.]

M. KAPEL

1569. Quantitative analysis of aromatic hydrocarbons in the 2 to 25-micron infra-red region. J. M. Martin, jun., R. W. B. Johnston and M. J. O'Neal, jun. (*Anal. Chem.*, 1954, **26** [12], 1886-1889).—Through the combined use of KCl and NaCl optics, application of i.r. spectroscopy to the quant. analysis of aromatic hydrocarbons was extended to cover the range 2 to 25 μ . The hydrocarbons studied were mainly the individual aromatic compounds having boiling points in the C_9 boiling range (295° to 330° F). The method described made possible the analysis of individual aromatics boiling up to 330° F on two fractions prepared by distillation. Standard deviation was $< \pm 0.45$ per cent. for any of the individual components.

G. P. Cook

1570. Rapid spot tests for identification of diphenyl, *o*-, *m*- and *p*-terphenyl(s), and certain other polyphenyls. L. Silverman and W. Bradshaw (*Anal. Chem.*, 1955, **27** [1], 96-99).—Formaldehyde-sulphuric acid reagent was investigated as a means of identifying polyphenyls individually or after separation by filter-paper chromatography. When dissolved in cyclohexane, as little as 3 μ g of diphenyl or 2 μ g of the terphenyls can be detected, as they all have specific colour reactions in this medium. Diphenyl can also be detected in the presence of *p*- and *m*-terphenyl. Higher polyphenyls such as quaterphenyl, quinquephenyl and sexaphenyl can also be detected. The test may be used successfully in conjunction with u.v. spectroscopy to follow the separation of polyphenyls by chromatographic or other means.

G. P. Cook

1571. Method for the rapid determination of xylene in printing-shop air. M. Niszczyski and Z. Grabowski (*Ochrona Pracy*, 1954, **8** [2], 57-59; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 32,919).—Xylene vapour is absorbed on silica gel saturated with a mixture of conc. H_2SO_4 and formaldehyde. The xylene turns the gel brown, 0.05 mg giving a marked colour. The colour is measured by means of a visual colorimeter, and the amount of xylene is determined by comparison with standards. The error is 0.01 mg per litre. The xylene concn. in air should not exceed 0.1 mg per litre.

E. HAYES

1572. Quantitative infra-red determination of trace impurities in solids using fractional crystallisation technique. Determination of catechol and resorcinol in quinol. C. C. Bard, T. J. Porro and H. L. Rees (*Anal. Chem.*, 1955, **27** [1], 12-15).—Increased sensitivity is attained in i.r. spectroscopic analysis by concentration of impurities relative to major constituents by fractional crystallisation techniques. When applied to the determination of catechol and resorcinol in quinol at the 0.1 per cent. level, standard deviations were found to be ± 0.015 for catechol and ± 0.008 for resorcinol. Methyl cyanide was used as solvent and the limit of detection was calculated to be 0.01 per cent. for both isomers. The resorcinol absorption band at 10.4 μ and the catechol band at 7.85 μ were used.

G. P. Cook

1573. Detection of surface-active phenol ethers with sulphuric acid and formaldehyde. M. J. Rosen (*Anal. Chem.*, 1955, **27** [1], 111-114).—Surface-active agents containing an active benzenoid nucleus, such as *O*-substituted alkylphenols and monosulphonated diphenyls, may be detected by the dark red colour produced when they are treated with conc. H_2SO_4 and formaldehyde. Colour reactions of fifty-two commercial surface-active agents with the reagents are listed.

G. P. Cook

1574. Spectrophotometric determination of α -naphthol in β -naphthol utilising differences in reaction rates. J. S. Parsons, W. Seaman and J. T. Woods (*Anal. Chem.*, 1955, **27** [1], 21-24).—The method depends on the higher rate of reaction of 1-naphthol than of 2-naphthol with diazotised 2-naphthylamine-5:7-disulphonic acid in strongly acid conditions. A partial separation of the two is made by precipitating most of the 2-naphthol from alkaline soln. by addition of acid, leaving all of the 1- and a little of the 2-compound in the filtrate. The reagent is added to this soln. at a carefully controlled temp. and the absorbancy is measured at 485 $m\mu$ after an exact time of reaction. With the conditions of time, temp. and acidity chosen, only a little of the 2-naphthol reacted. The standard deviation calculated for fourteen samples in duplicate over the range 0.07 to 0.35 per cent. of 1-naphthol was ± 0.004 per cent.

G. P. Cook

1575. Spectrophotometric determination of benzanthrone and 2:2'-dibenzanthronyl. K. B. Whetsel (*Anal. Chem.*, 1954, **26** [12], 1974-1977).—Samples containing benzanthrone (I) and 2:2'-dibenzanthronyl (II) are dissolved in conc. H_2SO_4 and the absorbance is measured at 374 and 550 $m\mu$. The I and II contents are calculated from these absorbancies. Application of the method to crude samples gave a standard deviation of ± 0.4 to ± 0.8 per cent. for I and of ± 0.7 to ± 1.1 per cent. for II. Recoveries ranged from 97.2 to 100.2 per cent. The principal disadvantages are errors caused by the background absorption of some samples and the necessity of testing each batch of H_2SO_4 before use.

G. P. Cook

1576. Potentiometric titration of very weak acids. Titration with hydroxides in non-aqueous media using glass-calomel electrode system. V. Z. Deal and G. E. A. Wyld (*Anal. Chem.*, 1955, **27** [1], 47-55).—Very weak acids were determined potentiometrically by titration with alcoholic KOH or tetrabutylammonium hydroxide soln. in ethylenediamine and dimethylformamide as solvents. In general, dimethylformamide was found to be the most suitable solvent, because it facilitated reading of the inflexion and did not have a large blank correction, but ethylenediamine was used to distinguish very weak acids, such as phenol, from stronger acids. The method was applied to alkylphenols, dihydropyridines, polyphenolic compounds, phthalic acids, di- and tri-alkyl phosphites and phosphorous and phosphoric acids. Satisfactory precision was attained when the method was applied to mixtures of phenol and stronger acids.

G. P. Cook

1577. Colorimetric determination of *o*-hydroxyphenylacetic acid in samples from penicillin fermentations. S. C. Pan (*Anal. Chem.*, 1955, **27** [1], 65-67).—The method is based upon that of Stoughton (*J. Biol. Chem.*, 1936, **115**, 293) and involves the conversion of phenols into *p*-nitrophenol, which exhibits a bright yellow colour when the soln. is neutralised with alcoholic ammonia. This colour is measured with a 420- $m\mu$ filter. Interfering substances in penicillin fermentations were found to give colour intensities so low that the effect on the result was negligible. When applied to fermentation media, extraction with pentyl acetate was adopted, and recoveries, assuming extraction efficiency in each case as 86 per cent., ranged from 93.1 to 101.5 per cent. As little as 3 μ g of *o*-hydroxyphenylacetic acid can be determined.

G. P. Cook

cation-exchange column (Amberlite IR-120), which is finally washed with water (200 ml). The eluate, free from MoO_4^{2-} and VO_3^- , is boiled for 5 min. under reflux, cooled and titrated with 0.1 N NaOH (phenolphthalein). **II** is treated similarly and the sum of the two titrations minus a blank of 0.4 ml represents the soda equiv. of all acids present in the original aluminate soln. After titration, the eluate is diluted to 250 ml with water and aliquots (100 ml each) are taken for SO_4^{2-} (Ba^{++} pptn.) and Cl^- (Ag^+ pptn.) determinations that are carried out by standard gravimetric methods. With the use of given equations, the difference of the soda equiv. of total acids and that of H_2SO_4 plus HCl gives the equiv. of organic acids. Results are given for aluminate soln.; reproducibility is claimed to be satisfactory.

D. A. PANTONY

1561. Chromatography of carboxylic acids on a silica gel column with a benzene-ether solvent system. D. S. Kinnory, Y. Takeda and D. M. Greenberg (*J. Biol. Chem.*, 1955, **212** [1], 379-383).—A column-chromatographic method is described for the separation of organic acids in which 0.05 N H_2SO_4 on silica gel is used as the stationary phase and benzene-ether as the solvent system. The method separates citric, α -oxoglutaric, succinic, fumaric, malic, acetic, propionic, butyric, pyruvic, α -oxopyruvic, α -oxovaleric and lactic acids. The recoveries are 80 to 100 per cent.; most are > 90 per cent. The solvent paper used prevents esterification of the acids and gives sharp peaks on the elution curve. The sensitivity of the method permits detection of 2 micro-equivalents of each acid. The acid fractions are located with methyl red, and are titrated with 0.001 N NaOH with phenol red as indicator.

J. N. ASHLEY

1562. The determination of dissociation constants of dibasic acids. H. Irving, H. S. Rossotti and G. Harris (*Analyst*, 1955, **80**, 83-94).—Existing methods for determining the Brønsted dissociation constants K_1 and K_2 of dibasic acids are discussed critically. The variation of optical density with pH for polybasic acids is discussed mathematically and, by a new treatment of the function derived for dibasic acids, a method is developed in which the co-ordinates of the maxima (or minima) and points of inflexion in the experimentally determined graph of absorbancy against pH are used for solutions containing the same total concn. of reagent. Applications of the method to the determination of the dissociation constants of the sparingly soluble reagents 5-nitroso-oxine, 8-hydroxyquinazoline, 8-hydroxy-2:4-dimethylquinazoline and 5-hydroxy-quinoxaline are described. It is shown that values of dissociation constants may also be obtained from the dependence on pH of other physical properties of the system.

A. O. JONES

1563. Reaction of deoxy sugars with anthrone. L. H. Koehler (*Anal. Chem.*, 1954, **26** [12], 1914-1916).—Red colours, with anthrone-sulphuric acid, were given by 2-deoxy-D-glucose, 2-deoxy-D-ribose and 2-deoxy-D-xylose, in contrast to the blue-green colours exhibited by fully hydroxylated sugars. Deoxypentoses showed greatest absorbance at 550 and 560 $\text{m}\mu$ and deoxyglucose at 520 $\text{m}\mu$. By using different heating times and concn., characteristic reaction rates and colour intensities were obtained.

G. P. COOK

1564. Identification of organic compounds. VIII. Micro-identification of alkyl halides, O-alkyl and N-alkyl groups by paper chromatography. M.

Večeřa and J. Gasparič (*Coll. Czech. Chem. Commun.*, 1954, **19**, 1175-1178).—A method is described for the conversion of alkyl halides into the corresponding thiuronium salts and the identification of these by paper chromatography, the spots being developed with bromocresol green. Substances containing O- and N-alkyl groups can be converted into the corresponding alkyl halides, and then treated similarly. In contrast to previous methods, this requires only 1 to 3 mg of sample, and enables mixed ethers and mixtures of alkyl halides to be identified. Isomeric alkyl groups cannot be distinguished in this way. [This is a translation into English of a paper that was published originally in *Chem. Listy*, 1954, **48**, 1360.]

M. KAPEL

1565. Determination of hydroxymethyl groups in 1:2-glycols and related substances. J. C. Speck, jun., and A. A. Forist (*Anal. Chem.*, 1954, **26** [12], 1942-1944).—The method is based on the oxidation of hydroxymethyl groups by IO_4^- , with measurement of the formaldehyde produced after reducing IO_4^- and excess of IO_4^- with SO_3^{2-} . The formaldehyde is determined by the formation of the coloured formaldehyde-chromotropic acid dye and measurement of the absorbance at 570 $\text{m}\mu$. The precision in the analysis of thirty-eight glucose samples was $< \pm 1.1$ per cent. and results were good with a variety of polyhydroxy compounds. Maltose gives high values.

G. P. COOK

1566. Determination of methylhydrazine. H. McKennis, jun., and A. S. Yard (*Anal. Chem.*, 1954, **26** [12], 1960-1963).—A study of the reaction of methylhydrazine with *p*-dimethylaminobenzaldehyde in aq. H_2SO_4 is presented. The compound formed is highly coloured and the reaction forms the basis of a micro-method for the determination of methylhydrazine; a wavelength of 458 $\text{m}\mu$ is the most suitable for spectrophotometric measurement. Some amines interfere with the determination as well as hydrazine itself. The oxidation of methylhydrazine by acidic IO_4^- follows the stoichiometry of hydrazine oxidation and forms the basis for the determination of larger quantities of methylhydrazine.

G. P. COOK

1567. Detection of beta-hydroxyethylamines by pyrolysis with sodium chloroacetate. M. J. Rosen (*Anal. Chem.*, 1955, **27** [1], 114-116).—Pyrolysis of β -hydroxyethylamines with sodium chloroacetate gives acetaldehyde as the decomposition product. The acetaldehyde is detected by the blue colour it gives when absorbed by a soln. of sodium nitroprusside containing diethanolamine. The colour reactions of forty-four amines and nitrogen-containing surface-active agents after pyrolysis with sodium chloroacetate are listed.

G. P. COOK

1568. Polarographic investigation of the cysteine-cystine system. II. The polarography of cystine. M. Kalousek, O. Grubner and A. Tockstein (*Coll. Czech. Chem. Commun.*, 1954, **19**, 1111-1122).—In view of the anomalous behaviour of cysteine and cystine in various potentiometric and colorimetric procedures, as well as the discrepancies in the values quoted for the oxidation potential of the cysteine-cystine system, this system was investigated polarographically. The system is an irreversible one, so that its apparent oxidation potential has no real significance. [This is a translation into Russian of a paper that was published originally in *Chem. Listy*, 1953, **47**, 1143.]

M. KAPEL

1569. Quantitative analysis of aromatic hydrocarbons in the 2 to 25-micron infra-red region. J. M. Martin, jun., R. W. B. Johnston and M. J. O'Neal, jun. (*Anal. Chem.*, 1954, **26** [12], 1886-1889).—Through the combined use of KCl and NaCl optics, application of i.r. spectroscopy to the quant. analysis of aromatic hydrocarbons was extended to cover the range 2 to 25 μ . The hydrocarbons studied were mainly the individual aromatic compounds having boiling points in the C_9 boiling range (295° to 330° F). The method described made possible the analysis of individual aromatics boiling up to 330° F on two fractions prepared by distillation. Standard deviation was $< \pm 0.45$ per cent. for any of the individual components.

G. P. Cook

1570. Rapid spot tests for identification of diphenyl, *o*-, *m*- and *p*-terphenyl[s], and certain other polyphenyls. L. Silverman and W. Bradshaw (*Anal. Chem.*, 1955, **27** [1], 96-99).—Formaldehyde-sulphuric acid reagent was investigated as a means of identifying polyphenyls individually or after separation by filter-paper chromatography. When dissolved in cyclohexane, as little as 3 μ g of diphenyl or 2 μ g of the terphenyls can be detected, as they all have specific colour reactions in this medium. Diphenyl can also be detected in the presence of *p*- and *m*-terphenyl. Higher polyphenyls such as quaterphenyl, quinquephenyl and sexaphenyl can also be detected. The test may be used successfully in conjunction with u.v. spectroscopy to follow the separation of polyphenyls by chromatographic or other means.

G. P. Cook

1571. Method for the rapid determination of xylene in printing-shop air. M. Niszczyski and Z. Grabowski (*Ochrona Pracy*, 1954, **8** [2], 57-59; *Referativnyi Zh. Khim.*, 1954, Abstr. No. 32,919).—Xylene vapour is absorbed on silica gel saturated with a mixture of conc. H_2SO_4 and formaldehyde. The xylene turns the gel brown, 0.05 mg giving a marked colour. The colour is measured by means of a visual colorimeter, and the amount of xylene is determined by comparison with standards. The error is 0.01 mg per litre. The xylene concn. in air should not exceed 0.1 mg per litre.

E. HAYES

1572. Quantitative infra-red determination of trace impurities in solids using fractional crystallisation technique. Determination of catechol and resorcinol in quinol. C. C. Bard, T. J. Porro and H. L. Rees (*Anal. Chem.*, 1955, **27** [1], 12-15).—Increased sensitivity is attained in i.r. spectroscopic analysis by concentration of impurities relative to major constituents by fractional crystallisation techniques. When applied to the determination of catechol and resorcinol in quinol at the 0.1 per cent. level, standard deviations were found to be ± 0.015 for catechol and ± 0.008 for resorcinol. Methyl cyanide was used as solvent and the limit of detection was calculated to be 0.01 per cent. for both isomers. The resorcinol absorption band at 10.4 μ and the catechol band at 7.85 μ were used.

G. P. Cook

1573. Detection of surface-active phenol ethers with sulphuric acid and formaldehyde. M. J. Rosen (*Anal. Chem.*, 1955, **27** [1], 111-114).—Surface-active agents containing an active benzenoid nucleus, such as *O*-substituted alkylphenols and monosulphonated diphenyls, may be detected by the dark red colour produced when they are treated with conc. H_2SO_4 and formaldehyde. Colour reactions of fifty-two commercial surface-active agents with the reagents are listed.

G. P. Cook

1574. Spectrophotometric determination of α -naphthol in β -naphthol utilising differences in reaction rates. J. S. Parsons, W. Seaman and J. T. Woods (*Anal. Chem.*, 1955, **27** [1], 21-24).—The method depends on the higher rate of reaction of 1-naphthol than of 2-naphthol with diazotised 2-naphthylamine-5:7-disulphonic acid in strongly acid conditions. A partial separation of the two is made by precipitating most of the 2-naphthol from alkaline soln. by addition of acid, leaving all of the 1- and a little of the 2-compound in the filtrate. The reagent is added to this soln. at a carefully controlled temp. and the absorbancy is measured at 485 $m\mu$ after an exact time of reaction. With the conditions of time, temp. and acidity chosen, only a little of the 2-naphthol reacted. The standard deviation calculated for fourteen samples in duplicate over the range 0.07 to 0.35 per cent. of 1-naphthol was ± 0.004 per cent.

G. P. Cook

1575. Spectrophotometric determination of benzanthrone and 2:2'-dibenzanthronyl. K. B. Whetsel (*Anal. Chem.*, 1954, **26** [12], 1974-1977).—Samples containing benzanthrone (I) and 2:2'-dibenzanthronyl (II) are dissolved in conc. H_2SO_4 and the absorbance is measured at 374 and 550 $m\mu$. The I and II contents are calculated from these absorbancies. Application of the method to crude samples gave a standard deviation of ± 0.4 to ± 0.8 per cent. for I and of ± 0.7 to ± 1.1 per cent. for II. Recoveries ranged from 97.2 to 100.2 per cent. The principal disadvantages are errors caused by the background absorption of some samples and the necessity of testing each batch of H_2SO_4 before use.

G. P. Cook

1576. Potentiometric titration of very weak acids. Titration with hydroxides in non-aqueous media using glass-calomel electrode system. V. Z. Deal and G. E. A. Wyld (*Anal. Chem.*, 1955, **27** [1], 47-55).—Very weak acids were determined potentiometrically by titration with alcoholic KOH or tetrabutylammonium hydroxide soln. in ethylenediamine and dimethylformamide as solvents. In general, dimethylformamide was found to be the most suitable solvent, because it facilitated reading of the inflexion and did not have a large blank correction, but ethylenediamine was used to distinguish very weak acids, such as phenol, from stronger acids. The method was applied to alkylphenols, dihydric phenols, polyphenolic compounds, phthalic acids, di- and tri-alkyl phosphites and phosphorous and phosphoric acids. Satisfactory precision was attained when the method was applied to mixtures of phenol and stronger acids.

G. P. Cook

1577. Colorimetric determination of *o*-hydroxyphenylacetic acid in samples from penicillin fermentations. S. C. Pan (*Anal. Chem.*, 1955, **27** [1], 65-67).—The method is based upon that of Stoughton (*J. Biol. Chem.*, 1936, **115**, 293) and involves the conversion of phenols into *p*-nitrophenol, which exhibits a bright yellow colour when the soln. is neutralised with alcoholic ammonia. This colour is measured with a 420- $m\mu$ filter. Interfering substances in penicillin fermentations were found to give colour intensities so low that the effect on the result was negligible. When applied to fermentation media, extraction with pentyl acetate was adopted, and recoveries, assuming extraction efficiency in each case as 86 per cent., ranged from 93.1 to 101.5 per cent. As little as 3 μ g of *o*-hydroxyphenylacetic acid can be determined.

G. P. Cook

1578. **cycloHexylamine**. British Standards Institution (B.S. 2534 : 1955, 9 pp.).—The material must be colourless and miscible with H_2O (1 vol. to 19 vol.) at $15^\circ C$; the specific gravity, distillation range, residue on evaporation and amine content by titration are prescribed, with methods for their determination.

H. P. PAGET

1579. **Micro-determination of bromine or chlorine in N-halogenated imides**. M. Z. Barakat and M. F. Abd El-Wahab (*Anal. Chem.*, 1954, **26** [12], 1973-1974).—The method is based on the liberation of I from KI in aq. acid medium by N-halogenated imides. Micro-quantities of N-bromosuccinimide and N-chlorosuccinimide can be determined by this method, because they are good oxidising agents and are quant. reduced to corresponding imides by I^- in aq. acid medium. The error of the method is $< \pm 2$ per cent. and as little as $5 \mu g$ can be detected.

G. P. COOK

1580. **Determination of active hydrogen atoms [in organic compounds]**. I. M. McAlpine and P. A. Ongley (*Anal. Chem.*, 1955, **27** [1], 55-58).—The Zerevitinoff method of determination of active hydrogen atoms in organic compounds is examined, particularly for the effects of solvent, temp. of reaction and nature of the active methylene groups in the substance under examination. The determination is carried out under standard conditions at ordinary temp. and at 50° to 60° , 100° and $170^\circ C$, and in one of the following solvents: ether, dipentyl ether, anisole or pyridine. Results of active hydrogen determinations under various conditions for approx. 120 compounds are presented; in general, higher temp. leads to higher results owing to higher solubility, agitation and expulsion of occluded gases, but with 2-nitroaniline only are results abnormally high at the higher temp. Except for increased solubility and temp. limitations due to b.p., solvent effects are negligible. Activating groups are used to interpret unexpectedly high results for certain classes of compound, but chelation and steric hindrance are regarded as having negligible effect.

D. A. PANTONY

1581. **Infra-red absorption of the aldehydic C-H group**. S. Pinchas (*Anal. Chem.*, 1955, **27** [1], 2-6).—Various aldehydes, particularly substituted benzaldehydes, were measured in the 3000 to 2600- cm^{-1} region. The aldehydic C-H group usually absorbs at about 2720 cm^{-1} , but for some ortho-substituted benzaldehydes this band rises considerably. The effect is tentatively attributed to a new kind of H-bonding, which involves the polar aldehydic H atom. Other characteristic bands in this region were also observed and their origins are discussed.

G. P. COOK

1582. **Direct method for the determination of methoxy group in the presence of borohydrides**. A. P. Alexander, P. G. Bourne and D. S. Littlehale (*Anal. Chem.*, 1955, **27** [1], 105-107).—A quant. method for the determination of the methoxy group in borohydrides is based on the oxidation of methanol to formic acid with a standard soln. of ceric ammonium nitrate. The excess of Ce^{IV} is then back-titrated with standard arsenite to the first trace of pink. An accuracy within ± 0.5 per cent. is attained.

G. P. COOK

1583. **Micro-determination of methylenedioxy or combined formaldehyde groups**. M. Beroza (*Anal. Chem.*, 1954, **26** [12], 1970-1973).—The method of Bricker and Johnson (*Ind. Eng. Chem., Anal. Ed.*,

1945, **17**, 400) for the determination of combined formaldehyde with chromotropic acid-sulphuric acid was modified to obtain results that more closely approach theoretical values. By this procedure, an absorbance equivalent of 0.75 to 1.08 moles of formaldehyde is obtained per mole of methylenedioxy group. The recovery of formaldehyde per compound averaged 98 per cent. as against 82 per cent. by the unmodified method. Application to 64 compounds gave results that were reproducible and accurate.

G. P. COOK

1584. **Iodimetric method for estimating acetate and the acetyl group**. D. Köszegi and J. Simonyi (*Acta Chim. Hung.*, 1954, **5** [1-2], 33-42).—The acetic acid liberated from acetates or from hydrolysed acetyl compounds with syrupy phosphoric acid is steam-distilled in a modified Kögl-Postowsky apparatus into an aq. suspension of $BaCO_3$. After being boiled for 5 to 10 min. and then cooled, the liquid is made up to a known vol. An aliquot containing the barium acetate is filtered off, a known excess of 0.05 N $K_2Cr_2O_7$ is added together with some 0.1 N NaOH soln., and the soln., after boiling for a short time, is again made up to a known vol. An aliquot is filtered and the excess of $K_2Cr_2O_7$ is determined iodimetrically with 0.05 N $Na_2S_2O_3$ soln. Good agreement is shown with the theoretical results when known acetate and acetyl samples are analysed by this method; the results are better than those obtained by a parallel acidimetric determination of the acetic acid. [This is a translation into German of a paper originally published in *Magyar Kem. Foly.*, 1954, **60** [8], 231.]

J. H. WATON

1585. **Amperometric method for mercaptan sulphur in hydrocarbons**. M. D. Grimes, J. E. Puckett, B. J. Newby and B. J. Heinrich (*Anal. Chem.*, 1955, **27** [1], 152-154).—The method presented is based on that by Kolthoff and Harris (*Brit. Abstr. C*, 1946, 161). Liquid samples are dissolved in ammoniacal acetone and are titrated with standard $AgNO_3$ and mercaptan S from gaseous samples is absorbed in an excess of $AgNO_3$ and the excess of Ag^+ is titrated with standard dodecyl mercaptan. The average deviation was 1 p.p.m. for gaseous hydrocarbons containing mercaptan S in the range 0 to 100 p.p.m., and 3 p.p.m. for gaseous hydrocarbons containing mercaptan S in the range 0 to 400 p.p.m. Organic sulphides, disulphides, thiophen and tetraethyl-lead do not interfere, nor does free S in amounts less than 0.001 per cent.

G. P. COOK

1586. **Spectrographic analysis of petroleum products and related materials**. L. L. Gent, C. P. Miller and R. C. Pomatti (*Anal. Chem.*, 1955, **27** [1], 15-17).—A new method for the preparation of samples in the spectrographic determination of relatively large quantities of metals and P in various materials is described. A small quantity of the sample is burned on a large bed of graphite powder containing CuO as a buffer and internal standard, and the resulting dry powder is thoroughly mixed. Portions of this mixture are placed into cratered electrodes by tamping and are subjected to d.c. arc excitation for 60 sec. Results agreed well with those from chemical analysis, being generally within ± 10 per cent. Used and unused lubricating oils, additive concentrates, greases, sludges and deposits can be analysed by this technique.

G. P. COOK

1587. Bomb-volumetric method for [determining] sulphur in refined petroleum products. R. E. Kreider and J. G. Foulds (*Anal. Chem.*, 1954, **26** [12], 1983-1985).—The method is based on the oxidation of the sample in a Parr oxygen bomb, reduction of the SO_2 with HI and iodimetric titration of the resulting sulphide. The accuracy is ± 2 per cent., but the method is not satisfactory for oils containing Ba, Se or N in significant amounts. G. P. COOK

1588. Application of catalytic desulphurisation to group-sulphur analysis of petroleum fractions. R. N. McCoy and F. T. Weiss (*Anal. Chem.*, 1954, **26** [12], 1928-1933).—Methods are described for the group-sulphur analysis of various petroleum fractions, including light and heavy distillates, lubricating oils, crude oils, residues and shale oils. Selective catalytic decomposition is used to differentiate non-thiophenic from thiophenic S, thiophen being decomposed over alumina at 450°C to H_2S , while the other compounds are stable under these conditions. Titration of the H_2S potentiometrically with AgNO_3 provides a rapid means for the determination of non-thiophenic S. Thiophenic S is calculated from the difference between the total S content of the sample and the non-thiophenic S. Recoveries of H_2S are generally > 90 per cent. and the methods are sensitive to ≈ 0.001 per cent. of S. G. P. COOK

1589. Determination of tetraethyl-lead in gasoline by X-ray fluorescence. F. W. Lamb, L. M. Niebylski and E. W. Kiefer (*Anal. Chem.*, 1955, **27** [1], 129-132).—The X-ray fluorescence method has been successfully applied to the determination of tetraethyl-lead in petrol. Analysis of forty-six samples covering the range 0.1 to 6.0 ml of tetraethyl-lead per gallon of sample gave a standard deviation of ± 0.28 ml per gallon. The error due to S was very small and that due to possible petrol additives such as P was negligible. The time required for one analysis was from 5 to 10 min. G. P. COOK

1590. Recognition and differentiation of the various types of chemical fibres. P. A. Koch (*Fibres*, 1954, **15**, 405-409).—A simple scheme for the identification of synthetic fibres is outlined. L. VALENTINE

1591. Analysis of coloured papers. J. Navarro Sagristá (*Afinidad*, 1954, **31**, 325-330).—The paper is successively extracted with H_2O , ethanol and other solvents, and the dyeing properties of the extracts for cotton and wool are examined. This gives some indication of the class of dyestuff, e.g., acid or basic. Paper-chromatographic separation of the extracts is carried out to determine the number of dyestuffs present. Reduction tests carried out on the paper serve to indicate the chemical type. Treatment of the extracts with each of the conc. acids H_2SO_4 , HCl and HNO_3 , and observation of the appearance of the original material under ultraviolet light give some clue as to the individual dyestuffs present. Special tests are carried out for mineral colours. L. A. O'NEILL

1592. Determination of moisture in [wood] pulp by the Karl Fischer method. W. Funasaka, M. Kawano and T. Kijima (*Japan Analyst*, 1953, **2** [3], 196-198).—Experimental conditions for the determination of water in pulp by the Karl Fischer method are examined. The complete extraction of water is achieved by digesting the sample (≈ 0.5 g) in pure methanol (30 ml) for 45 min. with occasional stirring. The results agree well with those by

drying methods, within an error of < 3 per cent. (relative). K. SAITO

1593. Determination of free sulphur in light paraffin oils by the Sommer test. I. G. E. Mapston. II. A. Albert (*Erdöl u. Kohle*, 1954, **7** [12], 826-829).—The authors discuss discrepancies in their observations (cf. *Anal. Abstr.*, 1954, **1**, 3029).

A. R. PEARSON

1594. Analysis of lubricating oil by thermal diffusion and mass spectrometry. F. W. Melpolder, R. A. Brown, T. A. Washall, W. Doherty and W. S. Young (*Anal. Chem.*, 1954, **26** [12], 1904-1908).—Application of the thermal diffusion process to the separation of a light lubricating oil into specific hydrocarbon types is described. Mass and u.v. spectrometry were used to analyse the thermal diffusion fractions, in which a total of sixteen different hydrocarbon types were identified and determined. In general, provided that prior separation of paraffins and aromatics by silica gel is made, the thermal diffusion process will concentrate the following types in varying degrees:—(i) normal paraffins from isoparaffins, (ii) isoparaffins from condensed cycloparaffins, (iii) monocycloparaffins from non-condensed di- and tri-cycloparaffins, (iv) condensed dicycloparaffins from condensed polycycloparaffins, (v) free phenyls from arylcycloparaffins and polynuclear aromatics, (vi) arylcycloparaffins and free naphthyls from diphenyls, fluorenes and tricyclic aromatics. G. P. COOK

1595. Determination of additive elements in lubricating oils by emission spectrographic methods. E. L. Gunn (*Anal. Chem.*, 1954, **26** [12], 1895-1899).—Additive Ca or Ba in the lubricating-oil sample are determined by a carbon-matrix method with Co oleate as the internal standard. Electrodes are loaded with the matrix mixture and are subjected to high-voltage spark discharge. The relative accuracy of the method is $\approx \pm 5$ per cent. for Ba and ± 8 per cent. for Ca in synthetic blends. The Ba 3891.8-Co 3894.1 and the Ca 3179.3-Co 3409.6A line pairs were used in these determinations. Additive P is determined by a porous cup technique, the oil being introduced into the spark zone by seepage. High-voltage spark excitation is used and a C line is measured as internal standard. The P 2535.6 and C 2582.9A line pair is used. The relative accuracy is $\approx \pm 6$ per cent. on synthetic blends over the range 0.01 to 0.05 per cent. of P. G. P. COOK

1596. Spectrographic method for analysing lubricating greases. C. W. Key and G. D. Hoggan (*Anal. Chem.*, 1954, **26** [12], 1900-1902).—The spectrographic method described provides rapid and accurate means of determining Al, Ca, Li, Na and Ba in lubricating greases. A mixture of 2-ethylhexoic acid, Sr 2-ethylhexoate, Co 2-ethylhexoate, heavy naphtha, pentyl acetate and lubricating grease can be blended with a mineral oil to produce a homogeneous liquid, which is transferred from a porcelain boat by a rotating disc to the discharge gap of a high-voltage spark in an inert atmosphere. The metal content is determined by reference to standard working curves and the max. deviation in percentages for ten analyses of each element were: Li, $+13$ to -19 ; Ca, $+4.8$ to -4.7 ; Na, $+4.0$ to -5.0 ; Ba, $+10.1$ to -4.7 ; and Al, $+5.8$. G. P. COOK

1597. Recent advances in the analysis of plastics. J. Haslam (*Chem. Age*, 1954, **71**, 1297-1303).—Recent advances and particular problems in the

analysis of plastics are discussed. The analysis of polyamides, methacrylate polymers, vinyl chloride polymers, phenolic and urea-formaldehyde resins and plasticisers are among the subjects treated.

N. E.

1598. Semi-quantitative analysis of Buna N phenolic [resin] blends by the infra-red spectra of their pyrolysates. F. F. Bentley and G. Rappaport (*Anal. Chem.*, 1954, **26** [12], 1980-1982).—Polymer blends and co-polymers yield pyrolytic products, the i.r. spectra of which reflect the composition of the polymer blends and co-polymer ratios. On application of the method to several known blends of Buna N phenolic resin it appears that the phenolic-resin content of such blends can be estimated within ± 2 per cent. in the range 0 to 33 per cent.

G. P. Cook

1599. Determination of elementary sulphur [in vulcanised rubber] by an isotopic dilution method. S. Ikeda and S. Kanbara (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75** [12], 1308-1311).—The application of an isotopic dilution method to the determination of elementary S co-existing with sulphides that are liable to decompose or to exchange sulphur atoms (mercaptobenzothiazole, dibenzothiazolyl disulphide, dibenzyl tetrasulphide, etc.) is studied. The measurement of the radioactivity must be carried out accurately (error < 1 per cent.), taking good care of the geometry of the sample. The sample is dissolved in benzene at room temp. and a known amount of radioactive S (in benzene) is added to it. Most of the benzene is removed by gentle evaporation beneath an infra-red lamp with a gentle flow of N. Alcohol is added to the conc. soln. (1 to 2 ml) to ppt. S, which is again dissolved in benzene. The same procedure is repeated 3 or 4 times to produce pure S, which is eventually oxidised to sulphate with Br, in water, and pptd. with BaCl₂. The ppt. is collected on a small piece of filter-paper and the radioactivity is measured. The amount of the elementary S in the initial sample can be calculated from the difference of the specific radioactivity. This method is suitable for the determination of S in acetone extracts of vulcanised rubber.

K. SAITO

1600. Detection of some antioxidants in some vulcanised rubber stocks. R. A. Hively, J. O. Cole, C. R. Parks, J. E. Field and R. Fink (*Anal. Chem.*, 1955, **27** [1], 100-103).—A method is presented for the isolation and detection of antioxidants in vulcanised rubber. Separation is accomplished with the use of three chromatographic schemes with alumina of two activities as adsorbent. Identification is effected by use of m.p. determinations, u.v. spectra, chromatographic-fraction number and i.r. spectral data. The technique was mainly applied to the separation and identification of Santoflex B, B-L-E (high temp. reaction product of diphenylamine and acetone), NN-diphenyl-*p*-phenylenediamine and N-phenyl-2-naphthylamine.

G. P. Cook

1601. Analysis of polybutadienes and butadiene-styrene co-polymers by infra-red spectroscopy. J. L. Binder (*Anal. Chem.*, 1954, **26** [12], 1877-1882).—Amounts of *cis*-1:4, *trans*-1:4 and 1:2 additions in polybutadienes, and styrene in butadiene-styrene co-polymers, can be directly determined by measuring band intensities at 14.7, 10.34, 10.98 and 14.29 μ , respectively. The analysis for styrene content of butadiene-styrene co-polymers gives results within 1 per cent. of those by refractive index methods.

From the analysis, quant. information about the effect of polymerisation variables on the micro-structures of polybutadienes and butadiene-styrene co-polymers may also be obtained. G. P. Cook

See also Abstracts 1511, 1523, 1604.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

1602. Measurement of total body water with deuterium oxide and phenazone. H. Ljunggren (*Acta Physiol. Scand.*, 1955, **33** [1], 69-82).—The deuterium oxide and phenazone methods of estimating total body water are compared by carrying out simultaneous determinations on two healthy men over a period of two months. Deuterium oxide is determined, after distillation of plasma water, together with known standards, by a gradient tube method with white spirit-bromobenzene mixtures. The accuracy obtained is ± 0.0017 per cent., the method thus being as accurate as the falling-drop method. The error caused by distillation is insignificant. The deuterium spaces (variability 1.8 to 2.0 per cent.) are more consistent than the phenazone spaces (variability 4.5 to 5.4 per cent.), probably owing to the error of ≈ 4 per cent. in estimating the zero-time concn. of phenazone. The deuterium spaces are greater than the phenazone spaces; the former probably over-estimate the true vol. of total body water owing to exchange of deuterium with labile hydrogen, and the latter under-estimate the vol. owing to protein binding of phenazone.

C. E. SEARLE

1603. A katharometric method for measuring helium in expired air. J. B. Hickom, E. Blair and R. Frayser (*J. Clin. Invest.*, 1954, **33**, 1277).—After breathing a mixture of equal parts of helium and oxygen for 15 min., the subject is switched to tank oxygen. The expired air is dried and freed from CO₂ and continuously analysed for He. The He is estimated with a katharometer, consisting of a Gow-Mac R.C.T. thermal-conductivity cell, with a sealed reference cell and an R.C.T. control unit. The output is measured on a Leeds and Northrup potentiometer of 0 to 64-mV range. This arrangement will estimate up to 3 per cent. of He (standard deviation, ± 0.04 per cent.) and gives a 95 per cent. response to a change in He concentration in 20 sec.

H. WIGGINS

1604. The micro-estimation of nitrogen by means of a diffusion cell. H. Wüst (*Klin. Wochschr.*, 1955, **33** [7-8], 185).—In this supplement to the earlier report (*Klin. Wochschr.*, 1954, **32**, 660) the introduction is recommended of a small stirrer, operated by a rotating magnet, into the central acid chamber of the diffusion cell to speed up the absorption of the NH₃ liberated in the peripheral chamber. Final titration can be carried out after 4 to 5 hr. at 80° C.

G. W. CAMBRIDGE

1605. The determination of calcium in serum by flame photometry. R. W. R. Baker (*Biochem. J.*, 1955, **59** [4], 566-571).—An internal-standard flame-photometric method in which an acetylene-air flame is used, is described for the determination of Ca, Na and K in serum, with dilution as the only pre-treatment of the sample. Use of an

acetylene - air flame ensures max. output of energy in the Ca bands, and the intensity of the light, although very low can be measured with a photoconductive cell or by means of photomultiplier apparatus. The results are obtained rapidly with an error $< \pm 2$ per cent. J. N. ASHLEY

1606. Some errors in the determination of calcium in aged blood serum eliminated by flame photometry. P. S. Chen, jun., and T. Y. Toribara (*Anal. Chem.*, 1954, **26** [12], 1967-1968).—The direct measurement of Ca in aged blood serum by flame photometry of acidified soln., from which protein has been removed by trichloroacetic acid, eliminates most of the errors that occur in the calcium oxalate pptn. technique. G. P. COOK

1607. Interference of sulphhydryl groups in analysis of urinary mercury, and its elimination. I. M. Weiner and O. H. Müller (*Anal. Chem.*, 1955, **27** [1], 149-150).—The Hg in the mersalyl-cysteine complex, which contains a Hg-S bond, was found to be more difficult to determine quant. than either the Hg in mersalyl or inorganic Hg; the same difficulty was experienced in the determination of Hg in the urine of dogs treated with mersalyl. The urinary Hg is therefore believed to exist in a form analogous to the mersalyl-cysteine complex. To deal with this, modifications in the method of Kozelka (*Brit. Abstr. C*, 1948, 102) were made and include (a) higher digestion temp., produced by adding $(\text{NH}_4)_2\text{SO}_4$ to the mixture and (b) a two-hour period of chlorine flow at 150 ml per min. With these modifications, the method gives results accurate to 1 μg over the range 9.5 to 57 μg . G. P. COOK

1608. Isolation and determination of zinc compounds in biological material. G. I. Kudymov (*Aptekhnos Delo*, 1954, **3** [6], 16-23).—In the determination of Zn (1 to 5 mg) in biological material, satisfactory results are obtained by destroying organic matter with H_2SO_4 and HNO_3 and then titrating the Zn against $\text{K}_4\text{Fe}(\text{CN})_6$ soln. with diphenylamine as indicator. E. HAYES

1609. A rapid procedure for the determination of lead in blood or urine in the presence of organic chelating agents. S. P. Bessman and E. C. Layne (*J. Lab. Clin. Med.*, 1955, **45** [1], 159-166).—In the method described, organic matter is destroyed by wet oxidation and the lead then determined colorimetrically as the dithizone complex. Calcium ethylenediaminetetraacetate, 0.5 per cent. in urine or 2.5 per cent. in blood, does not interfere. Twelve determinations on the blood of patients with no history of exposure to lead gave up to 43 μg per 100 ml with a mean of 18.2 ± 11.2 . Duplicate assays are recommended. W. H. C. SHAW

1610. A new method for the simultaneous micro-estimation of iron and copper in body fluids. F. Umland and F. G. Weyer (*Klin. Wochschr.*, 1955, **33** [9-10], 237-238).—The method is based on the formation of the oxines of copper and iron, the former showing an absorption maximum at 410 $\mu\mu$ and the latter showing peaks at 370, 465 and 580 $\mu\mu$. Serum (10 ml) is freed from protein by treatment with 6 N HCl (5 ml) for 10 min. followed by 20 per cent. aq. trichloroacetic acid (10 ml). After centrifuging, the supernatant fluid (20 ml) is placed in a separating funnel and a 1 per cent. solution of oxine in 10 per cent. acetic acid (0.1 ml) is added. The

mixture is brought to between pH 5 and pH 6 by conc. aq. NH_3 (2.4 to 2.5 ml), and acetate buffer at pH 5.4 (5 ml) is added. The mixture is shaken for 2 min. with two 2-ml portions of chloroform. The chloroform emulsion is centrifuged for 5 min., the supernatant aqueous phase is removed by suction and the extinction of the chloroform phase is determined at 410 and at 580 $\mu\mu$, with the use of a chloroform blank solution. The following formulae are applied: $E_{410} \times 13.7 = \mu\text{g}$ of Fe per ml of chloroform and $(E_{410} - 0.93 E_{580}) \times 11.0 = \mu\text{g}$ of Cu per ml of chloroform. [4 ml of chloroform extract \equiv 8 ml of serum.] G. W. CAMBRIDGE

1611. Paper chromatography of iron complexes of porphyrins. T. C. Chu and E. J.-H. Chu (*J. Biol. Chem.*, 1955, **212** [1], 1-7).—The iron complexes of uro-, copro-, haemato-, deuter-, meso- and protoporphyrins in the form of corresponding haemin, haematin or haematin acetate are separated by reverse-phase paper chromatography with water-propanol-pyridine as the solvent system and silicone (Dow-Corning No. 550) as the stationary phase. A simplified lutidine-water system is described for determination of the number of carboxyl groups of haemins and free porphyrins. J. N. ASHLEY

1612. Paper-chromatographic analysis of porphyrin isomers. R. Kehl and B. Günter (*Hoppe-Seyl. Z.*, 1954, **297** [3-6], 254-257).—Examination of stools, urine and erythrocytes by paper chromatography showed the presence of those porphyrin esters described by previous workers. A concn. of 1.5 μg in 10 ml of material is necessary for successful separation. *Procedure*—After acidifying with acetic acid, extract stools (5 g) or urine (10 ml) with ether and erythrocytes (2 ml) with ethyl acetate. Evaporate the extract under a reduced pressure of nitrogen. Dissolve the residue in methanol and esterify with dry HCl for 1 hr. under reflux. Add the product to 25 ml of chloroform and wash with distilled water until neutral, then evaporate *in vacuo*. Dissolve the residue in 0.03 ml of chloroform and apply the solution to paper. Develop in light petroleum-chloroform (11:8) at 19°C. Dry for 5 min. at 105°C and examine in u.v. light. Besides the red fluorescing porphyrins, the extracts of stools and urine will show yellow-brown and green bile pigments, while erythrocytes show dark haematin spots. Quant. estimation is carried out by elution with chloroform and treating the eluate with 7.8 N HCl for 1 hr. at room temp. The HCl concn. is brought to 5 per cent. before the colour is measured. F. POWELL

1613. Colorimetric determination of carboxy-haemoglobin in blood. I. Berka (*Pracovní Lékar.*, 1953, **5** [3], 133-138; *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 37,786).—The method is based on the reduction of PdCl_2 to metallic Pd by CO, the unchanged PdCl_2 being determined colorimetrically after the addition of diethyl-p-nitrosoaniline. The method is as precise and sensitive as the indirect method of Wennesland (*Acta Physiol. Scand.*, 1940, **1**, 50; 1941, **2**, 16) or the indirect method of Wolff (*Svenska Läkarsidn.*, 1941, **38**, 492, 622); it is also simpler and more suitable for routine analysis. E. HAYES

1614. The determination of sugar in blood and spinal fluid with anthrone reagent. J. H. Roe (*J. Biol. Chem.*, 1955, **212** [1], 335-343).—The determination of sugar in blood and spinal fluid with a modified anthrone reagent containing

thiourea (which greatly improves the stability and chromogenic property of the reagent) is described. Blood is deproteinised with tungstic acid, $\text{Ba}(\text{OH})_2$, ZnSO_4 , or 5 per cent. trichloroacetic acid, the preferable dilution being 1 in 10. Spinal fluid is diluted with water or with 5 per cent. trichloroacetic acid if large amounts of protein are present; tungstic acid cannot be used. The resulting liquids are treated with the anthrone reagent (containing 0.05 per cent. of anthrone, 1 per cent. of thiourea, and 66 per cent. v/v of H_2SO_4), the mixture is kept in boiling water for 15 min., and then cooled. A standard glucose solution is treated similarly, and the two solutions are compared in a photoelectric colorimeter with a 620-m μ filter.

J. N. ASHLEY

1615. The estimation of total protein content [of serum] from the paper electrophorogram. K. H. Kimbel and H. Bunte (*Klin. Wochschr.*, 1955, **33** [7-8], 187-188).—Total serum-protein content of 500 sera was determined by the biuret method (Gleiss and Hinsberg, *Brit. Abstr. C*, 1951, 298) and the relation between these values and the "extinction curve area," as determined by paper electrophoresis, was studied. The extinction-curve area does not give a measure of the total protein content. Statistical details are given. G. W. CAMBRIDGE

1616. Comparison of free and paper electrophoresis of serum proteins. I. R. Mackay, W. Volurlei and P. D. Goldsworthy (*J. Clin. Invest.*, 1954, **33**, 855).—Paper electrophoresis was performed with the apparatus of Grassman and Hannig, and of Durrum. A barbitone-sodium barbitone buffer (pH 8.6), ionic strength 0.1, was used since it had been found superior to barbitone-citrate, phosphate, citrate-phosphate, and citrate-phosphate-borate buffers (pH 7 to 9). Staining was performed with Amido black 10B and Azocarmine. Amido black was preferred, especially for bands of low protein concn. The dye concentration was measured on the Grassmann-Hannig photometer by using oil-soaked papers. A 1-mm \times 10-mm slit was used. A curve was obtained by plotting photometer reading (ordinate) against length along strip (abscissa). Planimeter measurements were made on the areas under the peaks, after perpendiculars had been dropped to the baseline from the lowest points between peaks. Schlieren diagrams, obtained from 1:4 sera in the same barbitone buffer, dialysed against buffer for 18 hr. at 5°C and run at 0°C to 1°C in a Pearson model of the Tiselius, and Perkin-Elmer model 38, electrophoresis apparatus, were treated similarly. Different results were obtained by the two techniques, especially for the β -globulin fraction, and no factor can be found to reconcile this difference. Paper electrophoresis was found to be a valid, reproducible and useful analytical method.

H. WIGGINS

1617. Colorimetric determination of plasma and serum albumin. D. Rubstein, E. Stelle, F. Ingenito and W. E. Reynolds (*J. Clin. Invest.*, 1954, **33**, 211-221).—To 0.9 ml of 0.2 M acetate buffer, at pH 6.2, is added 0.1 ml of serum or plasma, and 12.5 ml of a 10^{-4} M solution of 2-*p*-hydroxyphenylazobenzoic acid (a stock solution of 1×10^{-3} M adjusted to pH 6.2 with a minimum of buffer, before dilution with distilled water) are added to the solution. The volume of the mixture is made up to 15 ml. The colour is measured on an Evelyn photo-electric colorimeter with a 510 filter or a spectrophotometer set at 520 m μ against

a blank prepared from serum in the same way, but containing no dye solution. A calibration curve is prepared from a standard albumin solution. It is shown that the method is reproducible and a straight-line response is given up to an albumin concn. of 6.25 mg per tube. It is also shown that plasma fractions other than albumin do not change the optical density of the dye solution. Agreement was found with electrophoretic determinations of albumin, but the results were significantly lower than those given by a salting-out biuret method. H. WIGGINS

1618. Proteins. XXVI. Photometric analysis of protein hydrolysates. B. Keil (*Chem. Listy*, 1954, **48** [5], 725-734).—The development of the quant. paper chromatography of amino acids is reviewed and a novel method of quant. analysis of protein hydrolysates is described, in which the one-dimensional paper chromatogram is photographed in reflected light and the negative is evaluated photometrically. From the photometric curves, the amounts of individual amino acids in the hydrolysate are determined by planimetry. The method is illustrated by analyses of trypsinogen, chymotrypsinogen, bovine globin and fibrinogen, bovine and human serum albumin, ovalbumin and insulin hydrolysates. G. GLASER

1619. Phenylthiohydantoins in amino-acid analysis. [Preliminary report.] J. Sjöquist (*Biochim. Biophys. Acta*, 1955, **16** [2], 283).—Partition chromatographic methods have been described for the identification of the 3-phenyl-2-thiohydantoins of the products of the stepwise degradation of peptides (Sjöquist, *Acta Chem. Scand.*, 1953, **7**, 447; Edman, *Acta Chem. Scand.*, 1950, **4**, 283). The method has been applied to the quant. determination of the composition of complex amino-acid mixtures. The phenylthiohydantoins of natural amino acids show closely similar light-absorption curves, with sharp peaks at 269 m μ . A quant. yield of the phenylthiohydantoins can be secured from 10 to 20 μ g of each amino acid in extremely dilute solutions. Hence, automatic registration of the u.v. absorption at 269 m μ in the eluate from a chromatographic column gives the composition of the mixture. Hyflo Super-Cel was used as inert support and heptane-pentyl acetate-formic acid (90 per cent.) (14:3:1, by vol.) as the solvent. G. W. CAMBRIDGE

1620. The influence of buffering on the separation of dinitrophenylamino acids by means of paper chromatography. H. Iwinsky (*Hoppe-Seyl. Z.*, 1954, **27** [3-6], 194-198).—A systematic study of the effect of buffering on the separation of the dinitrophenyl derivatives of ten amino acids was undertaken. The filter-paper is soaked in the buffer and dried in air before use. Buffer is also used in place of water in preparing the solvent mixture for developing the chromatogram. A mixture of benzyl alcohol-ethanol-buffer (10:1:11) at pH 9 to 11 was the most satisfactory organic phase investigated. F. POWELL

1621. Separation of dinitrophenylamino acids by two-dimensional paper chromatography. T. Deutsch (*Magyar Kem. Foly.*, 1954, **60** [7], 205-206).—Ether-soluble dinitrophenylamino acids can be separated by two-dimensional paper chromatography with the use of 0.5 M sodium citrate (pH 6.4) and isobutanol-butyl acetate-HCl (2 per cent.) (5:3:2). P. HAAS

1622. Column-chromatographic separation of dinitrophenylamino alcohols for the purpose of estimating the terminal carboxyl groups of amino acids in peptides and proteins. W. Grassmann, H. Hörmann and H. Endres (*Hoppe-Seyl. Z.*, 1954, **296**, 208-213).—The free carboxyl groups are esterified and reduced with lithium borohydride to primary carbinol. After hydrolysis with acid, the terminal amino acids appear as amino alcohols. Treatment of the hydrolysate with fluorodinitrobenzene gives dinitrophenylamino acids (I) and dinitrophenylamino alcohols (II). Excess of fluorodinitrobenzene is removed by adding amino acid or 4-hydroxybenzoic acid. Ether removes II quant. from alkali carbonate soln. whereas I remains in the aqueous phase. Eight different II have been separated on a mixed column of silica gel and Celite (4 + 1) in a manner which permits quant. measurement. The separation is carried out by a series of solvents consisting of various mixtures of light petroleum, acetic acid, acetone and ethyl acetate. The chromatographic behaviour of II is similar to that of I, but the alcohols move more slowly, so the separation is better. Quant. measurement is carried out by reading the extinction at 366 m μ . F. POWELL

1623. Determination of cystine. E. M. Malikova (*Tr. Lav. Otd. V.N.I.R.O.*, 1953, [1], 273-279; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 34,241).—A routine colorimetric method for the determination of cystine depends on the reaction of the reduction product, cysteine, with tungstophosphoric acid to give a blue colour. A soln. of amino acids obtained by hydrolysis in 2.64 per cent. HCl soln. is decolorised by shaking with kaolin, filtered, treated with a soln. of Na₂SO₃ saturated with NaHCO₃ and then with Folin's reagent. The blue colour develops after 10 to 15 min. It is shown that in 2.5 per cent. HCl soln. only 3 to 4 per cent. of the cystine is adsorbed by the kaolin; it is not adsorbed by the humus substances in the hydrolysate. When animal charcoal is used for decolorising, it adsorbs 80 per cent. of the cystine. E. HAYES

1624. Colorimetric and iodimetric determination of methionine. I. Korpáczy (*Magyar Kém. Foly.*, 1954, **60** [8], 241-243).—McCarthy - Sullivan's colorimetric method for determining methionine (I) has been modified by replacing the mixture of conc. HCl and H₃PO₄ by 50 per cent. w/v H₂SO₄ and conc. H₃PO₄; ice-cooling is replaced by the use of tap-water. The resulting colour is stable for 24 hr. Extinction is measured in a Beckman spectrophotometer at 510 m μ . With the use of a calibration curve, the I content can be determined with an accuracy of 2.5 per cent. The iodimetric method of Albanesi *et al.* for semi-micro assays has the following modifications: (a) the vol. of soln. used is reduced to 5.0 ml, (b) the reaction time is increased to 6 hr., (c) the catalyst soln. is divided into two parts (i) 50 per cent. KI and (ii) ammonium molybdate containing 5 per cent. by wt. of H₂SO₄, to avoid blueing of the soln. immediately after titration, (d) the use of a 0.01 N Na₂S₂O₃ soln. for titrating the liberated iodine. P. HAAS

1625. A method for the extraction of steroids from blood. M. E. Lombardo, P. H. Mann, T. A. Viscelli and P. B. Hudson (*J. Biol. Chem.*, 1955, **212** [1], 345-351).—A method is described for the extraction of steroids from blood. It combines the processes of dialysis and extraction into one operation by use of the modified Hershberg and Wolf extractor (*J. Biol. Chem.*, 1941, **141**, 215). The inside phase of the dialysis system is blood-water-methanol

(1 + 1 + 1) and the outside phase is 60 per cent. aq. methanol. During dialysis the dialysate is continuously extracted with methylene chloride. Extraction is carried out for 48 hr., with fresh methylene chloride after 24 hr. to avoid exposing the steroid extract to prolonged heating. The method is reproducible, and there is a min. amount of manipulation. The blood extracts obtained are very small and relatively free from fat, pigments and cholesterol. Each extract is chromatographed directly and the steroids are located on the paper and are determined by standard methods.

J. N. ASHLEY

1626. Correction for colour differences between standards and urine extracts and their ketonic fractions in the Callow-Zimmermann reaction. H. P. Schedl, W. B. Bean, B. M. Stevenson and E. R. Schumacher (*J. Lab. Clin. Med.*, 1955, **45** [2], 191-214).—A detailed study is made of the determination of urinary 17-ketosteroids by the Callow-Zimmermann method and of the effects of applying the Girard procedure for separating crude urine extracts into ketonic and non-ketonic fractions on the resulting colour. Adherence to Beer's law and the use of formulae for correcting for interfering chromogens in both crude extracts and Girard-treated fractions are also investigated. It is concluded that only if a method of colour correction is used can the 17-ketosteroid content be expressed in terms of the standard, since the colours given by the sample and standard differ, and that the best results on crude urine extracts are obtained by correction, assuming that the non-17-ketosteroid chromogens have linear absorption between 425 and 595 m μ . Completely satisfactory results are not obtained by the use of a correction formula, and uncorrected results on the ketonic fractions may be misleading owing to the resulting colour differing from that of the standard and to the destruction of chromogenic matter in the Girard procedure.

W. H. C. SHAW

1627. Silica-gel micro-column for chromatographic resolution of cortical steroids. M. L. Sweat (*Anal. Chem.*, 1954, **26** [12], 1964-1967).—A silica-gel micro-column is described, which, when used in conjunction with fluorescent and phenylhydrazine analytical techniques, permits analysis of mixtures of pure steroids containing amounts as small as 0.25 μ g. The method has been applied successfully to the analysis of human, dog and rat blood, recoveries of corticosterone being > 90 per cent. and of 17-hydroxycorticosterone > 93 per cent.

G. P. COOK

1628. The function of the adrenal cortex in insulin regulation. [Separation of adrenal cortical hormones.] R. Froesch (*Schweiz. med. Wochschr.*, 1955, **85** [6], 121-127).—Extraction of carbohydrate-active adrenal cortical hormones from plasma was carried out by a slight modification of the Nelson and Samuels technique (*Anal. Abstr.*, 1954, **1**, 130) and the separated fractions were estimated by their reaction with sulphuric acid-phenylhydrazine (Porter and Silber, *Brit. Abstr. C*, 1951, 215). The elimination of errors due to the unspecific colour reactions with H₂SO₄ (Bayliss and Steinbeck, *Brit. Abstr. C*, 1953, 356) was achieved by the following technique. The material was taken up in methanol (0.6 ml) and one 0.2-ml portion was treated with dilute H₂SO₄ (0.3 ml) and another with 0.3 ml of the H₂SO₄-phenylhydrazine solution. After heating for 1 hr. at 60° C, the mixtures were cooled and cleared by shaking with ether (0.2 ml).

Before the extinction at 410 $m\mu$ was measured, tubes were heated to 70° C.

G. W. CAMBRIDGE

1629. The removal of non-steroidal pigments of urinary extracts by adsorption on charcoal. M. E. Lombardo, T. A. Viscelli, A. Mittelman and P. B. Hudson (*J. Biol. Chem.*, 1955, **212** [1], 353-360).—Activated charcoal removes most of the urinary pigments which interfere with the usual chromatographic methods for separation of steroids. A solution of the urinary extract in benzene-ethanol (2 + 3) is treated with charcoal, after which the steroids are eluted with the same solvent. Although free from pigments, the eluates have an amber colour which remains at the base line of application on the filter-paper in the usual chromatographic systems used, and sufficiently clean paper strips are obtained without further treatment. Steroidal artefacts are not formed under the given conditions.

J. N. ASHLEY

1630. The effect of urea on the inhibition of trypsin by soya-bean trypsin inhibitor. [Assay of trypsin activity.] K. Jacobsson (*Biochim. Biophys. Acta*, 1955, **16** [2], 264-267).—Enzyme solution (1 ml) containing trypsin was added to casein substrate (3 ml) (Kunitz, *J. Gen. Physiol.*, 1947, **30**, 291) and incubated for 3 hr. at 25° C. Trichloroacetic acid (0.33 N) (5 ml) was then added and, after centrifuging, the optical density of the supernatant fluid was determined at 280 $m\mu$. Reference curves were established by plotting the E_{280} for each batch of substrate against μg of trypsin. G. W. CAMBRIDGE

1631. Effects of an inhibitor of catalase on the induced formation of this enzyme in yeast. H. Chantrenne (*Biochim. Biophys. Acta*, 1955, **16** [3], 410-417).—In a study of the azide inhibition of catalase activity, the following method was used to determine catalase. The method, which is based on the reaction of titanium salts with H_2O_2 , eliminates errors caused by reducing substances present in yeast extracts that react with the permanganate used in the conventional method. The titanium reagent is prepared from saturated titanium sulphate in 2 N H_2SO_4 diluted (1 + 5) with 2 N H_2SO_4 . Yeast suspension (10 ml = 30 to 50 mg of solid) is treated with 0.15 M H_2O_2 soln. (0.4 ml). Samples (1 ml) are withdrawn after incubation for 0, 1, 2, 4 and 6 min. at 28° C, and mixed with titanium reagent (2 ml) in centrifuge tubes. A yellow colour develops immediately and, after centrifuging, the intensity of this colour is measured. Over a wide range, the extinction at 410 $m\mu$ is proportional to the concn. of H_2O_2 .

G. W. CAMBRIDGE

1632. Lipid-electrophoresis: its clinical value in relation to serum lipids and the influence of oral fat intake. H. W. Bansi, R. Th. Gronow and H. Redetzki (*Klin. Wochschr.*, 1955, **33** [5-6], 101-104).—The Grassman and Hannig paper-electrophoresis technique can be used for the separation of lipids from serum (0.03 ml) by the application of 110 V, for 14 hr., in barbitone buffer at pH 8.6. The lipids are stained by a modification of Schwan's method (*Scand. J. Clin. Lab. Invest.*, 1953, **5**, Suppl. 9), with the use of a half-saturated soln. of Sudan black B in 60 per cent. ethanol (staining time, 6 hr.) and subsequent washing for 20 min. in running conductivity water. Loss of intensity of colour on standing can be prevented by moistening with glycerol after drying the paper.

G. W. CAMBRIDGE

1633. A simple method for the determination of glycogen in liver. L. Gyermek and G. Fekete (*Nature*, 1955, **175**, 386).—Aliquots (2 to 3 g) of rat livers are homogenised with 2 to 3 ml of 10 per cent. trichloroacetic acid, which extracts the free physiologically variable glycogen. The homogenisation is completed by the addition of physiological saline. After filtration, 1.5 ml of ethanol are added to 1.2 ml of filtrate and the turbidity is measured in a colorimeter. The filtrate, suitably diluted with water, acts as a blank. In nine determinations, 103.6 \pm 3.85 per cent. recovery was attained.

E. J. H. BIRCH

1634. An enzymic method for the estimation of α -oxoglutaric acid and its application to the investigation of metabolic problems. W. Seitz, A. Englhart-Gölkel and I. Schaffry (*Klin. Wochschr.*, 1955, **33** [9-10], 228-234).—The method is based on the formation of glutamic acid from α -oxoglutaric acid and ammonia in the presence of the specific enzymes glutamic acid dehydrogenase and reduced diphosphopyridine nucleotide (DPNH), changes in the latter being determined at 366 $m\mu$. Heavy metals that might inhibit the reaction are removed by ethylenediaminetetra-acetic acid and the pH is maintained between 7.4 and 7.8 by a triethanolamine buffer. The test fluid (trichloroacetic acid filtrate of serum or a tissue extract) (5 ml) is treated with 3 M ammonium acetate (0.15 ml), 1 per cent. disodium ethylenediaminetetra-acetate (0.1 ml), 36 per cent. triethanolamine (pH 7.4) (0.6 ml) and DPNH solution, 10 mg per ml (0.05 ml), and the mixture is made up to 6 ml with distilled H_2O . After the initial extinction (I_0) has been measured at 366 $m\mu$, glutamic acid dehydrogenase solution (0.01 ml) is added, and, after 20 min., the extinction (I_{20}) is determined. The difference between I_0 and I_{20} multiplied by 42.3 gives μg of α -oxoglutaric acid per ml of test solution.

G. W. CAMBRIDGE

1635. Isolation of pyruvic and alpha-ketoglutaric acids from blood and tissues in the presence of carbon-14 acetate. E. Kvamme and L. Hellman (*Anal. Chem.*, 1954, **26** [12], 1995-1997).—Pyruvic and α -oxoglutaric acids were separated from labelled acetic acid by first forming the bisulphite addition complex and then removing the acetic acid from soln. by extraction with ether. The addition complexes are then dissociated with 10 per cent. Na_2CO_3 soln. and the free keto acids are treated with 2:4-dinitrophenylhydrazine in acid soln. The hydrazones formed are extracted into ethyl acetate, then into a soln. of Na_2CO_3 and finally into ethyl acetate again. The ethyl acetate is removed by vacuum distillation at low temp. and the residual hydrazones are separated by a chromatographic technique. More than 99.8 per cent. of contaminating acetic acid was removed and only 0.05 per cent. of carbon-14 acetate was present in the isolated keto acids. Recoveries of pyruvic and α -oxoglutaric acids from blood were 66 per cent.

G. P. COOK

1636. Colorimetric determination of ribose, deoxyribose and nucleic acid with anthrone. N. D. Gary and R. E. Klausmeier (*Anal. Chem.*, 1954, **26** [12], 1958-1960).—The anthrone reaction, under rigorously controlled conditions, can be used for the quant. determination of D-ribose and D-2-deoxyribose and their nucleic acids. The samples and anthrone- H_2SO_4 reagent are mixed in an ice-bath and the colour is developed by heating, in a boiling-water bath for 2.5 min. for ribose or ribonucleic acid, and for 10 min. for deoxyribose and its nucleic

acid. The colour is measured at 620 $m\mu$ for ribose and its nucleic acid and at 565 $m\mu$ for the deoxy compounds. The conditions chosen enable mixtures of the two classes to be determined. Recoveries from mixtures were 102 per cent. for the ribo compounds and 95.6 per cent. for deoxyribo-compounds. Hexoses interfere and must therefore be removed from the assay mixture.

G. P. COOK

1637. Adenosine pentaphosphate from commercial ATP (adenosine triphosphate). J. Sacks (*Biochim. Biophys. Acta*, 1955, **16** [3], 436).—Marrian (*Biochim. Biophys. Acta*, 1954, **13**, 278) reported that commercial ATP from ox liver contains up to one-third of the total adenine as adenosine tetraphosphate. Evidence is now found that adenosine tetra- and penta-phosphates are present in a preparation made from yeast. The nucleotides were adsorbed on Dowex-1 anion-exchange resin; AMP (monophosphate) was eluted with 0.002 *N* HCl, ADP (diphosphate) with 0.01 *N* HCl and ATP by 0.01 *N* HCl plus 0.04 *M* NaCl. When the optical density of the eluate fell below 0.05, the eluting solution was changed to 0.01 *N* HCl plus 0.2 *M* NaCl; two distinct peaks of optical density were observed which were shown to be due to the tetra- and penta-phosphates.

G. W. CAMBRIDGE

1638. The dephosphorylation of adenosine triphosphate to adenosine diphosphate during the contraction phase of the rectus muscle of the frog. [Identification of adenosine phosphates.] G. Lange (*Biochem. Z.*, 1955, **326** [3], 172-186).—Adenosine and its phosphates have been identified in extracts of frog muscle by high-tension electrophoresis (Turba, Pelzer and Schuster, *Hoppe-Seyl. Z.*, 1954, **296**, 97). Strips of paper 17 cm long were used, 60 V per cm at 1 mA per cm being applied for 2½ hr. Pyridine acetate buffer (0.1 *M*) at pH 6.5 was used and the inert cooling fluid was ice-cold toluene. Zones of the various fractions were located by photoprints by using the Markham and Smith technique (*Biochem. J.*, 1949, **45**, 294), and the fractions were eluted and checked against pure substances. The di- and tri-phosphates do not separate under the above conditions, but can be separated by high-tension electrophoresis in 2.5 per cent. sodium citrate - isopentanol buffer at pH 8.45. The spots are eluted and identified by further routine tests.

G. W. CAMBRIDGE

1639. Dissimilation of glucose-6-phosphate by *Azotobacter vinelandii* [Determination of triose and hexose.] L. E. Mortenson, P. B. Hamilton and P. W. Wilson (*Biochem. Biophys. Acta*, 1955, **16** [2], 238-244).—The use of simultaneous equations to determine the concentration of triose and hexose in mixtures after reaction with anthrone is proposed, as the extinction of hexose at 490 $m\mu$ is minimum when that of glyceraldehyde is maximum, whilst at 620 $m\mu$ the reverse is true (see also Willard, Merritt and Dean, "Instrumental Methods of Analysis," D. Van Nostrand Company, Inc., 1951). The following procedure was used. A mixture of glyceraldehyde (1.2 micromoles), glucose-6-phosphate (0.51 micromole) and ribose-5-phosphate (1.0 micromole) in a total volume of 1.5 ml was treated with anthrone reagent (4.5 ml) and heated in boiling water for 5 min. After the solution was cooled, the densities were determined in a Beckman spectrophotometer at 490 $m\mu$ and 620 $m\mu$ against a reagent blank. Ribose-5-phosphate gave no colour under these conditions and the estimated values for glyceraldehyde and glucose-6-phosphate

were 1.14 and 0.52 micromoles when 1.2 and 0.51 micromoles, respectively, were taken.

G. W. CAMBRIDGE

1640. Determination of oestrogens in stored urines of pregnancy. R. M. Anker (*J. Clin. Endocrinol.*, 1955, **15** [2], 211-214).—A shortened procedure for extraction is described, in which the partition method of Engel *et al.* (*Brit. Abstr. C*, 1951, 215) is combined with hydrolysis of the urine by boiling to remove *n*-butanol (used for storage) and then refluxing for 90 min. with toluene (20 per cent. v/v) and conc. HCl (15 per cent. v/v). The oestrogens are determined by Allen's modification of the Kober test (*Brit. Abstr. C*, 1950, 452). Urine specimens may be stored for two years at room temp. under a layer of *n*-butanol.

H. F. W. KIRKPATRICK

See also Abstracts 1681, 1689.

Drugs

1641. Application of ionophoresis to the separation of the alkaloids of opium. A. Mariani (*Pharm. Weekbl.*, 1955, **90** [4], 125-128).—Ionophoresis of HCl and Ca(OH)₂ extracts of the same opium in phosphate buffer at pH 6 on Munktel No. 20 paper for 8 hr., under a gradient of 5 V per cm, shows that alkaloids migrate towards the cathode at speeds proportional to K_B . The colorimetric reaction given by successive application of HIO₃, NaHCO₃ and FeCl₃ on a calcium hydroxide extract of opium after ionophoresis shows, besides the violet spot due to morphine, a grey spot that moves slowly and whose original material fluoresces in u.v. light. This may be the substance that interferes with the colorimetric determination of morphine with HIO₃ - NaHCO₃ - FeCl₃.

E. J. B. BIRCH

1642. Application of infra-red spectrophotometry to quantitative analysis in the solid phase. [Determination of atropine and hyoscyne.] R. S. Browning, S. E. Wiberley and F. C. Nachod (*Anal. Chem.*, 1955, **27** [1], 7-11).—The pressed potassium bromide pellet technique has been successfully applied as an aid in the quant. determination of atropine and hyoscyne by i.r. spectrophotometry. Recoveries from standard mixtures of the two alkaloids showed a mean value of 104 per cent. for atropine and 98.2 per cent. for hyoscyne. Difficulties encountered in the use of the technique are discussed as well as the reasons for only moderate accuracy with a complex commercial mixture.

G. P. COOK

1643. Determination of 7-dihydroxypropyltheophylline with periodic acid. A. Wickström and A. Valseth (*Ann. Pharm. Franç.*, 1954, **12** [7-8], 576-580).—The α -glycol group in 7-dihydroxypropyltheophylline (Glyphylline) (I) is oxidised quantitatively by periodic acid at 18° to 20° C in 5 min. to 6 hr., forming 1 mol. of formaldehyde and 1 mol. of 7-formylmethyltheophylline and reducing 1 mol. of HIO₄ per mol. of I. A 50 to 130-mg sample is dissolved in 5 ml of water, added to 20 ml of 0.05 *N* HIO₄ and left for 15 min. at \approx 20° C. Five ml of 2.5 *M* KHCO₃, 25 ml of standard sodium arsenite solution and 1 ml of 20 per cent. KI solution are added. The excess of arsenite is titrated, after 15 min., with 0.1 *N* iodine solution.

E. J. H. BIRCH

1644. Contributions to the analysis of rhubarb. VI. Anthraquinones. E. W. Neuhoft and H. Auterhoff (*Dtsch. ApothZtg.*, 1954, **94** [24], 541-544).—The methods of distinction of Chinese and

Rhapontic rhubarb are discussed. The paper chromatography of a number of samples of these rhubarbs is described and the results show that spots of characteristic R_F values (Rhapontic 0.29, and Chinese 0.035, 0.05 and 0.44) distinguish these drugs. For Chinese rhubarb it is found that ED_{50} can be expressed as ≈ 35.5 mg of total anthraquinones. Both the anthranol and anthrone glycosides in Chinese rhubarb, which give spots of R_F values 0.035 and 0.05, yield rhein on hydrolysis, (R_F 0.44), while the spots of R_F 0.12 and 0.64, which occur in both varieties, give on hydrolysis a spot of R_F 0.92 (frangula emodin or chrysophanic acid); therefore Chinese rhubarb after hydrolysis affords only two spots (R_F 0.44 and 0.92). Some colour reactions are given for rhaponticin and the colour with vanillin may be used for quant. estimation as follows: The drug is refluxed with ethanol (15 min.) and filtered. Paper chromatography of an aliquot portion of the diluted extract gives rhaponticin spots (recognised by u.v. light). These, on extraction with boiling methanol, give a soln. which on concn. and treatment of an aliquot part with 0.2 per cent. vanillin in 70 per cent. H_2SO_4 , followed by warming (water bath 1 min.) and cooling (15 min.) yields a soln. suitable for colorimetric estimation.

F. R. MUMFORD

1645. Photometric determination of capsaicin. L. Benedek (*Élelmészeti Ipar*, 1953, 7 [4], 123-127; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 32,928).—The photometric determination of capsaicin (I) is based on its reaction with $VOCl_3$, after interfering substances have been removed by extraction with kerosene and NaCl soln. A sample (4 g) of ground drug is dried at 50° C and shaken with 40 ml of acetone; after centrifuging for 10 min., 10 ml of deodorised kerosene (or kerosene which has been treated with 5 times its vol. of conc. H_2SO_4 for 24 hr. and then distilled, the fraction which boils below 220° C being collected) are added to 20 ml of the clear acetone soln., and the mixture is shaken for 5 min. with 10 ml of 5 per cent. aq. NaCl. After evaporation of the aqueous layer, the residue is extracted with acetone (10 + 5 ml) and the filtered extract is diluted with acetone to 13 ml [?]; 0.25 ml of HCl (sp. gr. 1.19) and 0.1 mg of NH_4VO_3 are added and the mixture is shaken for 20 sec. The colour is measured 2 min. after the commencement of shaking in a Pulfrich photometer fitted with filter S 72. The content of I (in mg) in 13 ml of soln. = $1.25 K - 0.125$, where K is the optical density. The intensity of the colour conforms to Beer's law, but decreases linearly with time. Because of incomplete removal of coloured interfering substances, lack of specificity of the reagent and the residual colour of the reagent, the calibration line cuts the ordinate at $K = 0.1$. Results obtained on various types of Hungarian pepper are given.

E. HAYES

1646. A defective test in the [French] Codex for the detection of arsenic in calcium gluconate. J. Soleil (*Ann. Pharm. Franç.*, 1954, 12 [7-8], 562-565).—The method prescribed in the French Pharmacopoeia (1949, p. 132) for detecting As in calcium gluconate gives a positive result for samples shown to contain no As. In the suggested alternative method organic matter is destroyed by heating with sulphuric and nitric acids, and the precipitated $CaSO_4$ is removed by filtration. The solution is then reduced in a Marsh apparatus and the AsH_3-H_2 stream is bubbled through 0.05 N iodine solution, in which the As is then detected

by Bougault's reagent, and determined iodimetrically in the precipitate.

E. J. H. BIRCH

1647. Determination of easily hydrolysable fructose units in dextran preparations. C. S. Wise, R. J. Dimler, H. A. Davis and C. E. Rist (*Anal. Chem.*, 1955, 27 [1], 33-36).—The dextran sample (> 5 g) is treated with 0.2 N H_2SO_4 (100 ml, or proportionally) at 70° C for 1 hr. The soln. is cooled and neutralised with 0.4 N $Ba(OH)_2$ (bromothymol blue). Sufficient ethanol is added to give an 85 per cent. v/v ethanolic soln., and the pptd. Ba^{++} salts and dextran are removed by decantation and centrifuging. The liquor is evaporated under vacuum and the dry residue is dissolved in water (1 or 2 drops); this soln. is examined by paper chromatography with butanol-pyridine-water (6:4:3, by vol.) as developing solvent. Fructose is located by means of urea- H_3PO_4 reagent [urea (3 per cent.) dissolved in $M H_3PO_4$ in 80 per cent. w/w aq. butanol, to which is added 5 per cent. v/v of ethanol. For the determination of the fructose, the chromatogram spots or dextran samples up to 60 mg in wt. are extracted with water (2 ml) and, together with a 60- μ g fructose standard and a reagent blank, are treated with anthrone reagent [0.125 per cent. w/v of anthrone in ethanol-conc. H_2SO_4 (3:5)] (8 ml). After 20 min. at 50° C, the soln. is chilled and its absorption measured at 620 $m\mu$ against the reagent blank. Alternatively, 500-mg samples are examined similarly with 0.1 per cent. resorcinol in ethanol in 7 N HCl soln., absorptions being measured at 505 $m\mu$. Analytical figures for eight dextrans or carbohydrate mixtures of known composition are given. Fructose gives 240 times the colour intensity of glucose in the same circumstances with either reagent.

D. A. PANTONY

1648. Microbiological assay on large plates. I. General considerations with particular reference to routine assay. K. A. Lees and J. P. R. Tootill (*Analyst*, 1955, 80, 95-110).—The problems and techniques involved in performing microbiological assays on large seeded agar plates with about 50 to 150 zones are discussed. The means whereby non-uniformity of response over such large areas is overcome are described and suitable methods are given for the simultaneous routine assay of several samples with a standard assay error of $\approx \pm 5$ per cent.

A. O. JONES

1649. Microbiological assay on large plates. II. Precise assay. K. A. Lees and J. P. R. Tootill (*Analyst*, 1955, 80, 110-123).—Methods of conducting precise large-plate microbiological assays suitable for relatively pure preparations of antibiotics or growth factors are described. In addition to the random experimental error associated with microbiological assay, inaccuracies may occur from inaccurate weighing and inaccurate dilution of the sample and standard preparations and from the presence of substances, other than the antibiotic under assay, that influence the zone size. The method presented allows these factors to be tested directly, and designs are given for the simultaneous assay of up to three unknowns with an assay standard error of ± 1 per cent.

A. O. JONES

1650. Isotope-dilution technique for determining benzylpenicillin in fermentation liquors. G. C. Ashton and M. C. Foster (*Analyst*, 1955, 80, 123-132).—A ^{14}C isotope dilution assay of benzylpenicillin in fermentation liquors is described. A known wt. of radioactive benzylpenicillin (the

label) is added to a known vol. of the broth sample and the penicillin is extracted with CHCl_3 and transferred from this extract into a phosphate buffer soln. To separate the benzylpenicillin from phenylacetic acid derived from precursors it is extracted from the phosphate buffer with pentyl acetate and converted into its isopropyl ether derivative (Trenner and Buhs, *J. Amer. Chem. Soc.*, 1948, **70**, 2897). This derivative is hydrolysed with alkali and the phenylacetic acid formed after acidification is extracted with cyclohexane and purified by crystallisation from light petroleum. Phenylacetic acid is similarly prepared by hydrolysis of the radioactive benzylpenicillin to determine the degradation of the label. The pure phenylacetic acid from the sample is subjected to radioactivity measurement and is compared with that prepared from the label. The dilution of the latter with the inactive benzylpenicillin originally present in the broth is thus determined. A. O. JONES

1651. Azaserine assay with *Kloechera brevis*. D. L. Kohberger, H. C. Reilly, G. L. Coffey, A. B. Hillegas and J. Ehrlich (*Antibiot. & Chemother.*, 1955, **5** [2], 59-63).—An adaptation of the filter-paper disc plate-type microbiological assay is described for the determination of the tumour-inhibiting antibiotic, azaserine (O-diazoacetyl-L-serine), with the yeast *Kloechera brevis* (Northern Regional Research Laboratory, U.S. Dept. Agric. Y-915) as test organism. The procedure, which has a sensitivity range of 0.3 to 15 μg per ml, is satisfactory for cultivation, fractionation and purification studies, although its usefulness in the estimation of low levels of azaserine in body fluids is limited by test sensitivity and by the tendency of urine components, particularly certain amino acids, to interfere with the inhibition of the yeast growth. W. H. C. SHAW

1652. Critical study of the [French] official test for liver extracts for oral use. G. Tixier and J. Neudörffer (*Ann. Pharm. Franç.*, 1954, **12** [9-10], 649-653).—Comments are made on the French official tests for moisture, amino nitrogen and vitamin-B₁₂ contents of liquid liver-extracts. It is concluded that (i) there is no parallelism between the therapeutic effects and the cyanocobalamin content of a preparation (from tests on rats); (ii) the method of the 1954 Supplement to the French Codex determines other growth factors, besides vitamin B₁₂, for the organism used; and (iii) the turbidimetric method in a cyanide medium with an *Escherichia coli* mutant is specific for cyanocobalamin. A modification of this method will be published shortly. (The paper has no experimental details.) S.C.I. ABSTR.

1653. Detection of chloroform and chloral hydrate in toxicological analysis. J. Kubalsi (*Acta Polon. Pharm.*, 1954, **11** [1], 39-45; *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 34,670).—Chloroform can be quantitatively removed from a saturated aqueous solution containing chloral hydrate by a stream of air at 20°C. The total chloroform plus chloral hydrate are first determined by the method of Stepanov (*Sudebnaya Khimiya*, 1951). The chloroform is then removed from a 1-ml aliquot and absorbed in a mixture of 0.5 ml of pyridine and 1 ml of 20 per cent. NaOH soln. The development of a rose colour in the absorption liquid serves as a qualitative test for chloroform. E. HAYES

1654. Iodimetric methods for the quantitative determination of phenolphthalein. A. I. Gengrinovich and I. Mansurkhanova (*Aptekhnoe Delo*, 1954, **3** [6],

9-12).—Add 10 ml of a 10 per cent. soln. of Na_2CO_3 to a weighed sample of phenolphthalein (0.05 to 0.15 g) and heat until soln. is effected; transfer the cooled soln. to a stoppered flask, add 15 to 50 ml of 0.1 N iodine soln. and shake; add 12 ml of 2 N HCl, 10 ml of ether and 1 to 2 ml of starch soln. and titrate the excess of iodine with $\text{Na}_2\text{S}_2\text{O}_3$. Instead of 0.1 N iodine, 0.1 N ICl in HCl soln. can be used, but, before acidification, 10 ml of 10 per cent. KI soln. are added. One ml of 0.1 N iodine or ICl \equiv 0.003977 g of phenolphthalein. In acid soln., the iodination of phenolphthalein is slow and not quant. Results obtained by the method on tablets and powders agree with those obtained by the U.S.S.R. Pharmacopoeia VIII method, in which the phenolphthalein is extracted with ethanol and weighed. Compared with both these methods, the bromimetric method gives high results, especially on tablets. E. HAYES

1655. Infra-red spectra of barbiturates. T. Canbäck (*Pharm. Weekbl.*, 1955, **90** [4], 116-118).—The i.r. spectra of a number of barbiturates in liquid paraffin are discussed and that of diallyl-barbituric acid is illustrated. The spectra show the same general shape between 3 and 8 μ . Methylation of ring nitrogen causes new bands to appear at 7.9, 8.4, 9.5 and 11.05 μ . Compounds containing the allyl group have bands at 6.06, 10.1 and 10.8 μ and, if Br is substituted for the middle hydrogen of this group, the bands are shifted 1 μ towards a longer wavelength. The benzene ring is shown by weak bands at 6.24 and 6.64 μ , and cyclohexenyl and cycloheptenyl by bands at \approx 11.9 μ . E. J. H. BIRCH

1656. Improved method for the separation of sulphonamides with the use of paper chromatography. J. Pucher (*Farmacia Polska*, 1954, **10** [1], 15-17; *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 34,676).—A method for separating various sulphonamides is described; the solvents used are a mixture of *n*-butanol, acetic acid and water (40:10:50), and *n*-butanol saturated with conc. aq. NH_3 soln. The paper is arranged so that the amount of surface in contact with the liquid is limited and the rate at which the liquid rises is reduced. E. HAYES

1657. A procedure for the assay of the sulphonamides, proposed for inclusion in the D.A.B. 6. K. Winterfeld, K. Bodendorf and P. Loth (*Dtsch. ApothZtg.*, 1955, **95** [5], 99-103).—A detailed description of the procedure and required specifications is described for the assay of sulphanilamide, sulphadimidine, sulphaguanidine, sulphathiazole and sulphathiourea, including quantitative and qualitative methods, solubilities, detection of heavy metals and moisture determination for each compound. G. R. WHALLEY

1658. Determination of chlorine and iodine in iodochlorohydroxyquin. J. A. C. van Pinxteren and M. E. Verloop (*Pharm. Weekbl.*, 1955, **90** [5], 145-149).—In the determination of Cl in iodochlorohydroxyquin by the U.S.P. XIV method, free Cl is lost during the oxidation with alkaline KMnO_4 , and the results are unsatisfactory. The following modified procedure gives satisfactory results. A sample (100 mg) of iodochlorohydroxyquin is gently boiled for 30 min. with a mixture of 20 ml of dil. H_2SO_4 (1 + 1), 40 ml of *N* KMnO_4 soln. and 10 ml of water in a 250-ml flask connected to a specially constructed receiver containing 16 ml of *N* NaOH soln. and 4 ml of a saturated soln. of SO_2 . The contents of the receiver are washed into a 250-ml Erlenmeyer

flask; 10 ml of 3 per cent. H_2O_2 soln. are added and the soln. is made acid with HNO_3 . Ten drops of a 1 per cent. ethanolic soln. of diphenylcarbazone and 15 ml of ether are added, and the chloride is titrated with 0.1 N $\text{Hg}(\text{NO}_3)_2$ until the ether layer becomes purple. The residue in the flask is cooled and sufficient of a 10 per cent. soln. of NaNO_2 is added to discharge the colour of the KMnO_4 and dissolve the MnO_2 residue; urea is added to remove excess of nitrite, and tartaric acid is added to remove any periodate formed. After 10 min., an excess of KI is added, and the liberated iodine is titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

E. HAYES

1659. Colorimetric method for quantitative micro-determination of quaternary ammonium compounds. J. Fogh, P. O. H. Rasmussen and K. Skadhauge (*Brauwissenschaft*, 1955, 8 [3], 57).—Indicators similar to bromocresol purple can react with quaternary ammonium compounds such as cetylpyridinium bromide, and colours are produced that are not associated with the indicator at any pH. By use of this reaction, a micro method for their determination has been developed.

Cetylpyridinium chloride solution (4 ml) containing up to 25 μg per ml is mixed with indicator solution (0.1 ml) and 0.5 N disodium phosphate (0.20 ml). A similar mixture is made up without the cetylpyridinium chloride and used as a blank. The intensity of the colour produced is measured in a Beckman spectrophotometer with 1-cm cuvettes at a wavelength of 620 m μ . The Beer-Lambert law has been shown to apply for concentrations up to 25 μg per ml. When dealing with coloured solutions, two similar solutions should be prepared, one as described above, and the other with an addition of a buffer solution (20 ml) consisting of 0.5 N disodium phosphate and 2 per cent. aq. Teepol; this second mixture serves as a blank.

The results are within certain limits independent of temperature, and not influenced by the presence of Ca, Mg, Fe^{++} , Fe^{+++} or Cu^{++} up to a concentration of about 1 per cent. Treatment of the glass apparatus with polymethacrylate (Plexiglas) can reduce the adsorption of the quaternary ammonium compounds on the glass surface. G. H. BAKER

1660. The quantitative determination of neoarsphenamine with the aid of colloidal metal hydroxides. E. Malec (*Roczn. Państw. Zakł. Hig.*, 1953, [2], 193-207, *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 34,672).—The composition of the ppt. formed by the interaction of various colloidal metal hydroxides with neoarsphenamine (I) are examined. $\text{Cr}(\text{OH})_3$ forms a compound $\text{R}_2\text{Cr}(\text{OH})_3 \cdot 20\text{H}_2\text{O}$ (mol. wt. = 1841), and $\text{Th}(\text{OH})_4$ forms $\text{R}_4\text{Th}_5\text{Th}(\text{OH})_{14} \cdot x\text{H}_2\text{O}$, where $\text{R} = \text{I}$. Except for $\text{Fe}(\text{OH})_3$, all the hydroxides investigated precipitate I quantitatively. With $\text{Fe}(\text{OH})_3$, I is oxidised. $\text{Th}(\text{OH})_4$ forms the least soluble ppt.

E. HAYES

1661. Determination of trivalent and total arsenic in the same sample, with special consideration of the evaluation of 3-amino-4-hydroxyphenylarsine oxide (Mapharsen). I. Boldizsár and I. Kerényi (*Acta Chim. Hung.*, 1954, 5 [1-2], 121-132).—When As^{III} and As^{V} are present together in inorganic compounds, the As^{III} is determined by titration with KBrO_3 . Before estimating the total As, Br^- is removed by heating for 30 min. with H_2SO_4 and H_2O_2 ; in this way, any loss of As^{III} as a volatile halide is eliminated. Additional experiments show that removal of Cl^- and I^- in a similar manner does not affect the estimation of total As. However, if

the As is covalently bound to an aromatic nucleus, only Cl^- and Br^- may be removed with H_2SO_4 - H_2O_2 without significant loss of As. As^{III} in 3-amino-4-hydroxyphenylarsine oxide cannot be estimated iodimetrically in the pH range 2.0 to 6.8, even in the absence of interfering decomposition products. If the sample is dissolved in 6 to 7 per cent. H_2SO_4 , then the estimation is possible even when interfering material is present. Before determining the total As with KBrO_3 , the I^- is removed by pptn. with 0.1 N AgNO_3 soln., as the H_2SO_4 - H_2O_2 method is inapplicable.

J. H. WATON

See also Abstracts 1577, 1607, 1672.

Food

1662. Simple photo-colorimetric method for the determination of reducing sugars. G. Janiček and J. Hrdlička (*Listy Cukrovarn.*, 1954, 70 [2], 27-32; *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 32,924).—Methods of determining reducing sugars are reviewed and a simple method based on the photo-colorimetric measurement of unconsumed Fehling's soln. is described. It is shown that the solutions used in the Fehling-Soxhlet, Allihn and Schoorl-Luff methods have colours that obey Beer's law. With Fehling-Soxhlet soln., the cooled reaction mixture is transferred to a cell and centrifuged, and the colour is measured without removing the ppt. of Cu_2O . Calibration curves are constructed from results obtained with pure glucose, maltose and lactose. Colourless sugar solutions are essential.

E. HAYES

1663. Determination of sugars in foodstuffs. L. Acker, W. Diemair and D. Pfeil (*Stärke*, 1954, 6, 241).—The carbohydrate constituents of malt extracts, starch syrups and other foodstuffs were determined by separation on a descending paper chromatogram, followed by colorimetric determination with anthrone-sulphuric acid (I). Glucose, maltose (II), maltotriose (III) and maltotetraose (IV) were determined separately, whilst sugars with higher mol. wt. were grouped with dextrins. The ratio of II to III and the content of IV are characteristic for the method of production. The procedure consisted in applying 0.01 ml of a 5 per cent. soln. (equivalent to 450 μg of dry carbohydrate mixture) to a paper strip and eluting with butanol-glacial acetic acid-water (4:1:5) for 24 hr. A test strip was developed with resorcinol-trichloroacetic acid and aniline phthalate. Removal of individual spots was carried out by dipping one end of the horizontal paper strip into water and collecting the first millilitre that dripped off at the other end by capillary action. The colour, developed after heating with I containing 0.2 g in 100 ml of H_2SO_4 , was measured at 620 m μ .

E. DUX

1664. Chromatographic determination of glutamic acid [in maize gluten]. Y. de Hemptinne and W. Vegult (*Fermentatio*, 1954, [4], 190-193).—The sodium salts of the amino acids obtained by the acid hydrolysis of maize gluten are dissolved in water (2 g in 500 ml), and the soln. is passed over Amberlite IRC-50 to convert the salts into free acids, and then over Amberlite IR-4B for selective adsorption of glutamic and aspartic acids. The amino-N of these two acids is determined as the difference between the amino-N in the original material and that not adsorbed by Amberlite IR-4B, by using the potentiometric titration method of Sørensen. The two adsorbed acids are eluted with 500 ml of 2 per cent. NaOH, and 100 ml of the

eluate, acidified with H_2SO_4 to pH 1 to 2, are boiled with an excess of $CuCO_3$ and filtered hot. The residue obtained after evaporation of the filtrate is dissolved in the minimum volume of water, and the Cu aspartate is pptd. by the addition of 40 ml of methanol and filtered off. The filtrate and methanol washings are evaporated to dryness, and the Cu glutamate is determined in an aq. solution of the residue by gravimetric determination of the Cu as CuS .

P. S. ARUP

1665. Determination of ionised calcium and magnesium in milk. G. Christianson, R. Jenness and S. T. Coulter (*Anal. Chem.*, 1954, **26** [12], 1923-1927).—A method for the determination of Ca^{++} and Mg^{++} in milk by cation exchange is presented. The activities of these ions are measured by determination of the quantity bound by a cation-exchange resin (Amberlite IR-100) equilibrated against milk, and are converted into Ca^{++} and Mg^{++} concn. by comparison with the quantities bound by the exchanger in equilibrium with standard soln. containing Na, K, Mg and Ca as chlorides. The apparent concn. of these ions in normal separated cows' milk at 22° to 25° C are 2.0 to 2.3 millimoles of Ca^{++} and 0.82 to 0.85 millimole of Mg^{++} per litre.

G. P. COOK

1666. Methods for the sampling and chemical analysis of acid casein. British Standards Institution (B.S. 1417: 1955, 16 pp.).—In this revised edition of the Standard published in 1948, uniform tests are prescribed for ascertaining the quality of acid casein and relating the analytical character to the manufacture of more standard grades of casein. The following tests are detailed in the specification: sampling, preparation of sample for tests, size of particle, determination of coarse particles of foreign matter, moisture (at 101° to 102° C for 5 hr.), ash (at 850° \pm 20° C), fat, total acidity (expressed as number of ml of 0.1 N NaOH to neutralise 1.0 g of sample), free acidity (expressed as lactic acid), pH value, iron (colorimetrically by *o*-phenanthroline), nitrogen, rate of solution and pH of solution in borax.

G. H. BAKER

1667. Identification of traces of isovaleric acid in butter adulterated with hydrogenated dolphin oil. G. D'Arrigo (*Olivi Min.*, 1955, **32** [1], 2-7).—Hydrogenated dolphin oil if present in butter is shown by the presence of isovaleric acid. The volatile acids are separated from butter by the technique employed for the determination of the Reichert - Meissl index. The liquid is allowed to stand \approx $\frac{1}{2}$ hr. and filtered, and the filtrate is neutralised with 0.1 N KOH soln. After suitable concentration, the soln. is analysed by ascending paper chromatography, *n*-butanol saturated with an equal vol. of 3 N $aq. NH_3$ being used as developer. The development takes \approx 10 hr., after which the chromatograms are allowed to dry for at least 30 min. in air. On spraying with a soln. containing 50 mg of bromophenol blue and 200 mg of citric acid in 100 ml of H_2O , the positions of the acids appear as blue spots on a yellow background. A description is given of the apparatus in which the determination is carried out. The method will detect \approx 0.075 per cent. of isovaleric acid in butter, and hence can reveal the presence of hydrogenated dolphin oil at concn. as low as 1.5 per cent.

J. H. WATON

1668. Determination of dissolved oxygen in beer. J. Hummel (*Brauwissenschaft*, 1955, **8** [1], 10-12).—The gasometric apparatus includes two aspirators (750 and 500 ml) connected through the bottom

outlets by a tube carrying a screw-clip. The larger aspirator carries at the top a vertical graduated tube, which ends in a glass tap. Through the lower stopper, a tube carrying a screw-clip leads to a glass tube, which will extend to the bottom of the beer bottle and passes through one hole of a stopper that fits the bottle. Passing through the second stopper-hole is the stem of a 50-ml tap-funnel. The large aspirator and all the tubes are filled with water. The beer bottle is cooled to 0° C and carefully opened; the stopper carrying the tap-funnel and tube is inserted and water is run from the large aspirator to drive out the air, a little of the beer being allowed to flow upwards into the funnel. After the water in the large aspirator and its graduated tube has been replaced with aq. 60 per cent. NaOH (with removal of air-bubbles), the beer in the bottle is heated to 60° C on a water bath during 30 to 40 min., with alternate shaking and opening of the screw-clip to connect with the aspirator. The bulk of the dissolved air is carried with the CO_2 and the froth into the aspirator, and measured in the graduated tube. The residual air in the bottle is indirectly determined by first absorbing all the CO_2 in aq. NaOH delivered from the tap-funnel (the connections with and between the aspirators being closed), and then by slowly opening the clip to the large aspirator and noting, on the graduated tube, the vol. of water required to fill the air-space in the bottle. This volume is added to the one previously observed. The oxygen content of the dissolved air decreases after keeping for a few hr. or after pasteurisation. The results agree well with results obtained by the application of the Rothchild and Stone colorimetric method (oxidation of K indigodisulphonate) to the testing of bottled beer. The advantages of routine control by the gasometric method are pointed out, and the connection between beer stability and low oxygen content is demonstrated by experiments.

P. S. ARUP

1669. Colour determination in wort and beer. II. E. Schubert (*Brauwissenschaft*, 1955, **8** [3], 50-57).—Experiments and results are described for the accurate determination of colour and turbidity in wort and beer, by means of a photocolourimeter of specified design incorporating colour filters. The experiments for the preparation of the turbidity curve being as yet incomplete, a further series of experiments for the determination of turbidity in wort and beer are described. The method is based on the difference in the turbidity between the filtered and unfiltered samples, using a Jena-glass frit, which has been shown not to retain any colouring matter. An accuracy of 0.5 per cent. has been reported.

G. H. BAKER

1670. Review of hop analysis methods. H. E. Weissler (*Amer. Soc. Brew. Chem., Proc. Ann. Mtg.*, 1954, 57-62).—This review covers the history of the A.S.B.C. Hop Sub-committee, the purposes of hop analysis, physical methods, chemical analysis and bacteriostatic methods. The Hop Analysis Methods currently used are those adopted by the Committee in 1942. New analytical methods for the determination of hop constituents are reviewed with particular reference to those of Howard (*J. Inst. Brew.*, 1953, **59**, 36). No experimental details are given. (38 references.)

S.C.I. ABSTR.

1671. Chromatographic detection of cinnamaldehyde in dessert wine and wine-containing drinks. H. Grohmann and F. H. Mühlerberger (*Z. Lebensmitt.-Untersuch.*, 1954, **99** [5], 361-367).—The presence

of cinnamaldehyde was proved by using hydrazine or benzidine, the sensitivity of the hydrazine reaction being increased in daylight by the addition of SnCl_2 . Losses by oxidation of the aldehyde, especially in a water-saturated atmosphere, are considerable. This can be remedied by the use of petroleum spirit (boiling range 110° to 140°C or 120° to 180°C) as a solvent (15 to 20 ml.). After the test solution has been running for 60 to 80 min., the paper is dried and hydrazine hydrochloride solution is applied. If a quartz lamp is not available, hydrazine and SnCl_2 are used with advantage. Benzidine was used in a second test. The method allows of the detection of 0.2 mg per litre of cinnamaldehyde, of vanillin and of other natural aromatic substances of wines to be separated and identified, and is claimed to be more sensitive than the organoleptic test.

S.C.I. ABSTR.

1672. Determination of purines in caffeine-containing drugs. H. Michl and F. Haberier (*Monatsh.*, 1954, **85** [4], 779-795).—Purines were isolated from a number of products, e.g., coffee, tea, cocoa beans, kola and maté, by grinding the powdered material with 20 per cent. conc. NH_3 and extracting in a Soxhlet with damp CHCl_3 (in the case of cocoa, after preliminary removal of fat). The resulting extracts were analysed by paper chromatography according to Michl (*Monatsh.*, 1952, **83**, 737) and individual purines were identified by colour reactions and determined by spectrophotometry; their apparent mobility was determined by electrophoresis (*loc. cit.*). The limit of detection was found to be 10^{-3} per cent.

P. HAAS

1673. New comparison solution for the estimation of sesame oil used as a detecting agent. B. Romani and G. Valentini (*Olii Min.*, 1955, **32** [1], 8).—The officially prescribed standard comparison soln. for testing for sesame oil in seed oils has disadvantages. The KMnO_4 - $\text{K}_2\text{Cr}_2\text{O}_7$ mixture does not give the exact shade of colour and is not stable. A more suitable and stable comparison soln. consists of 10 ml of 0.05 per cent. Bordeaux R soln., 0.10 ml of 5 per cent. $\text{K}_2\text{Cr}_2\text{O}_7$ soln. and 2 ml of liquid paraffin.

J. H. WATON

1674. Determination of chlorophyll in oil. R. C. Stillman (*J. Amer. Oil Chem. Soc.*, 1954, **31** [11], 469-472).—A spectrophotometric method for the determination of chlorophyll in oil is described. The results obtained with the use of three different instruments are compared, reliability of results is determined and standard deviations are calculated.

D. BAILEY

1675. Analytical methods and composition of fatty materials. R. W. Riemenschneider (*J. Amer. Oil Chem. Soc.*, 1954, **31** [11], 517-523).—The essential features and applications of analytical methods for determining fatty acid and glyceride composition are discussed. The methods for fatty acid composition include chemical methods, u.v. spectrophotometry and i.r. spectroscopy, and for glyceride composition, oxidation and crystallisation methods. Analyses of some common fats are reported. (54 references.)

D. BAILEY

1676. Determination of monoglycerides and glycerine in mixtures. M. Kruty, J. B. Segur and C. S. Miner, jun. (*J. Amer. Oil Chem. Soc.*, 1954, **31** [11], 466-469).—An improved method of determining monoglycerides and glycerol in mixtures is described. Both monoglycerides and glycerol in chloroform solution are oxidised by periodic acid

in methanol and the excess of periodic acid is determined in slightly alkaline solution by reduction to iodate with KI; the released I is determined with standard sodium arsenite solution. The glycerol alone is determined in the presence of monoglycerides by oxidation in a two-phase system of CHCl_3 and water with an aq. periodic acid solution and determination of the excess of periodic acid as before.

D. BAILEY

1677. Method of calculating fatty acid composition from ester fractionation analysis. E. W. Jones and M. A. Maclean (*J. Amer. Oil Chem. Soc.*, 1954, **31** [11], 473-475).—The calculations involved in ester fractionation analysis require the solution of sets of three simultaneous equations. Repeated solution of these equations is avoided by obtaining expressions for the proportions of the components. These expressions are presented and the construction of slide rules and nomograms for use in frequent analyses is outlined.

D. BAILEY

1678. Determination of peroxides in fats by the titanium method. C. Furmanek and K. Monikowski (*Roczn. Państw. Zchl. Hig.*, 1953, **4**, 447-457; *Referativnyi Zh.*, *Khim.*, 1954, Abstr. No. 38,239).—It is shown that Ti^{IV} reacts quant. to give a yellow colour only with those organic peroxides that can be hydrolysed to give H_2O_2 as one of the products. The iodimetric method of Drozdov and Starikova (*Myasnaya Industriya*, SSSR, 1951, [3], 52) gives satisfactory results; results obtained by the Lea method are 2 to 8 per cent. higher.

E. HAYES

1679. Chemical and microbiological methods in the examination of vitamin preparations. K.-E. Bonn (*Pharm. Weekbl.*, 1955, **90** [4], 97-111).—Samples of preparations of vitamins A and D are saponified and extracted with ether-ethanol. A chloroform solution of the vitamins is chromatographed on a column of starch (16 cm) covered by 6 cm of talc impregnated with SbCl_3 . The vitamin A remains on the column as a blue complex and the vitamin D is obtained quantitatively in the eluate. To an aliquot of the eluate is added a drop of SbCl_3 reagent and 0.5 ml of acetyl chloride, and the absorption is measured against a blank of CHCl_3 and acetyl chloride. The absorption is also measured without separation. A calibration curve is prepared and accuracy within ± 10 per cent. is attained if the actual titre is near the declared content. Ascorbic acid is determined by established colorimetric and iodimetric methods. The various B vitamins are determined microbiologically (nicotinamide is first hydrolysed to nicotinic acid). Discs of absorbent paper are soaked in the test or standard solutions and placed in a Petri dish containing the appropriate culture and medium and two standard and two test discs. The discs are incubated for 18 to 24 hr. at 37°C (30°C for adermine) and the diameters of the growth zones are measured. For thiamine, *Lactobacillus fermenti* A.T.C.C. 9338; for riboflavin, *Lactobacillus casei* A.T.C.C. 7469; for nicotinamide, nicotinic acid and calcium pantothenate, *Lactobacillus arabinosus* A.T.C.C. 8014; and for adermine, *Saccharomyces carlsbergensis* A.T.T.C. 4228, are used as the test organisms. The methods described are tested with a number of medicaments made up in different ways and the results are listed.

E. J. H. BIRCH

1680. Separation of vitamin B₁ in presence of fluorescent substances likely to interfere with its determination. Separation from sodium salicylate. L. Domange and S. Longueval (*Pharm. Weekbl.*,

1955, 90 [4], 119-121).—After preliminary experiments to determine the conditions, a sample containing $\approx 100 \mu\text{g}$ of vitamin B_1 is passed through a column (7.5 cm \times 8 mm) of Amberlite IRC-50, which has been regenerated with 4 per cent. NaOH and washed with water. Up to 100 mg of sodium salicylate are not retained on the column. The retained vitamin is eluted from the column by 0.5 N HCl (25 ml or until the eluate is acid) and estimated by measurement of its fluorescence. Less concentrated HCl does not elute all the vitamin.

E. J. H. BIRCH

1681. A rapid simple method for the determination of reduced, dehydro and total ascorbic acid in biological material. R. R. Schaffert and G. R. Kingsley (*J. Biol. Chem.*, 1955, 212 [1], 59-68).—Deproteinised blood or serum, or urine, is shaken vigorously with Norit (U.S.P. grade), and total ascorbic acid (L + dehydro) is determined in the filtrate by a modification of the 2:4-dinitrophenylhydrazine method. The procedure is then repeated, but without the treatment with Norit; this gives the amount of dehydroascorbic acid. The L-acid is then determined by difference. *Procedure*—The deproteinised filtrate or urine (4 ml) is treated with 1 drop of 10 per cent. thiourea in dil. ethanol (prepared by dissolving 10 g of thiourea in 50 ml of ethanol and 50 ml of water) and 2:4-dinitrophenylhydrazine (1 ml of a solution of 2 g in 100 ml of 9 N H_2SO_4). The mixture is kept in boiling water for exactly 5 min. for blood or serum (or 10 min. for urine or food). The mixture is then placed in ice and 85 per cent. H_2SO_4 (5 ml) is added drop by drop; the contents are mixed and, after keeping for 10 min., the optical density is read in a spectrophotometer against a control (prepared in exactly the same way except for omission of 2:4-dinitrophenylhydrazine) set at 100 per cent. light transmission at 515 $m\mu$.

J. N. ASHLEY

1682. Comparative study of the methods of Tillman and Roe for the estimation of ascorbic acid. I. Pennacchiotti (*An. Bromatologia*, 1954, 6, 359-363).—In fresh fruits and vegetables, when ascorbic acid and dehydroascorbic acid are present together and when little dioxogulonic acid has been formed, the colorimetric assay of Roe (2:4-dinitrophenylhydrazine in H_2SO_4 at 520 $m\mu$) is a satisfactory method for the assay of ascorbic acid.

L. G. L. UNSTEAD-JOSS

1683. Determination of ascorbic acid in mangaba (*Hancornia speciosa*). L. V. de Farias and B. Magalhães Neto (*Rev. Quim. Ind., Rio de Janeiro*, 1954, 23, 20-22).—The method for estimating vitamin C was based on direct titration with potassium iodate (*Ind. Eng. Chem., Anal. Ed.*, 1941, 13, 89) combined with the use of ascorbinase according to the modified technique of Tauber and Kleiner (*J. Biol. Chem.*, 1953, 110, 559). *Procedure*—To 1 ml of mangaba juice are added 1 ml of 5 per cent. KI solution and 2 ml of 2 N H_2SO_4 ; the mixture is titrated with 0.01 N iodate (starch endpoint). A further 1 ml of the same juice and 1 ml of acetate buffer at pH 6.0 are added, sufficient ascorbinase extract, prepared according to the method of Farias and Magalhães Neto (*An. Soc. Biol. Pernambuco*, 1953, 11) is added and the mixture is incubated at 38° C for 30 min. After this, 2 ml of 3 per cent. H_3PO_4 are added to inhibit the enzyme and the mixture is titrated with iodate as before. The difference in titration is a measure of true ascorbic acid; 1 ml of 0.01 N iodate \equiv 0.88 mg of ascorbic acid. Mangaba juice was found to con-

tain from 74 to 128 mg per 100 ml according to location and time of year.

H. PRITCHARD

1684. Determination of vitamin E (tocopherol) in natural substances containing vitamin E. B. Bencze (*Magyar Kém. Foly.*, 1954, 60 [9], 257-264).—The macrometric determination of tocopherol is effected by HNO_3 oxidation (Furler-Meyer reaction), the resulting red colour being measured photometrically (S 47 filter); the reaction is carried out in 96 per cent. ethanol with HNO_3 (sp. gr. 1.4). The tocopherol must be previously isolated by saponification with alcoholic KOH containing pyrogallol and subsequent extraction with light petroleum, the evaporated residue from which is used for oxidation. Steroids, if present, must be removed with digitonin. When using 0.5 to 20 mg, the limit of error is 1 to 3 per cent. With minute quantities of vitamin E (a few μg) the tocopherol-red is condensed with *o*-phenylenediamine in an acetic acid medium. The resulting phenazine derivative is adsorbed from light petroleum soln. on to a column of active alumina and eluted with a mixture of benzene and light petroleum. The purified compound is taken up in methanol-butanol mixture and its fluorescence is measured in a fluorimeter or, alternatively, the soln. is titrated in u.v. light against a standard soln. Limit of error \approx 10 per cent.

P. HAAS

1685. The assay of vitamin B_{12} in liver extracts. G. Tixier and J. Neudörffer (*Bull. Soc. Chim. Biol.*, 1954, 36 [8], 1173-1175).—Three methods of assay for vitamin B_{12} in liver extracts for oral administration are compared, two of which are turbidimetric, one with *L. leishmannii* (Skeggs, *J. Biol. Chem.*, 1948, 176, 1456) and the other with *E. coli* (Bürkholder, *Science*, 1951, 114, 459), and the paper-disc method (*Ann. Pharm. Franç.*, 1953, 11, 151). The precision of the turbidimetric methods is about \pm 3 per cent., but the error of the paper-disc method may be as high as \pm 50 per cent.

N. E.

See also Abstracts 1565, 1618, 1645.

Sanitation

1686. The colorimetric determination of silicate with special reference to sea and natural waters. J. B. Mullin and J. P. Riley (*Anal. Chim. Acta*, 1955, 12 [2], 162-176).—A detailed investigation of the molybdenum-blue reaction for SiO_3^{2-} provides the following optimum conditions for its analytical application. *Reagents*—(I) Acid ammonium molybdate soln.: dissolve 2 g of ammonium molybdate in 70 ml of water and 6 ml of conc. HCl, dilute with water to 100 ml and keep in a Polythene bottle. (II) Metol-sulphite soln.: dissolve 5 g of metol in a soln. of 3 g of Na_2SO_3 (anhyd.) in 240 ml of water, dilute to 250 ml and keep in a dark bottle. (III) Reducing agent: mix 100 ml of II with 60 ml of 10 per cent. w/v aq. oxalic acid and add, while cooling, 120 ml of 25 per cent. v/v H_2SO_4 , and dilute with water to 300 ml. *Procedure*—Treat the flasks to be used with a mixture of conc. H_2SO_4 and conc. HNO_3 (1 + 1) overnight, wash them with water and keep them wet. Add 20 ml of the sample, containing up to 60 μg of Si, to 3 ml of I. After 10 min., add 15 ml of III, dilute with water to 50 ml and set aside for 3 hr. Measure the optical density at 812 $m\mu$ with the use of a 1-cm, 3-in. or 6-in. cell according to the silicon content. Determine, and correct for, the reagent blank. Calibrate the method with aliquots of standard sodium silicate soln. containing 10 mg of Si per litre.

Sea-water causes a salt error, but a corrected optical density is expressed by $D_0 (1 + 0.00578x)$, where D_0 is the observed optical density and x is the concn. per cent. of Cl^- . Samples of sea-water should be diluted by one third with distilled water to improve precision. At a concn. of 0.2 p.p.m. of Si, the standard deviation is 0.48 per cent. No other ions present in natural water cause error. Fe^{+++} , Cu^{++} and F^- interfere when present in appreciable concn., but means of prevention are described. Error due to PO_4^{+++} is suppressed by the use of oxalic acid in III.

W. C. JOHNSON

1687. Application of ion-exchange resins to the analysis of water. II. M. V. Tovbin and F. G. Dyatlovitskaya (*Ukr. Khim. Zh.*, 1954, 20 [4], 434-437).—Water containing 0.4 to 5.5 milliequiv. per litre of SO_4^{--} and Cl^- is passed through a column of cationite resin, and free HCl plus H_2SO_4 in an aliquot of the filtrate is titrated with standard alkali. To 100 ml of water are added 5 to 7 ml of 0.1 N $\text{Ba}(\text{OH})_2$, the mixture is filtered, the filtrate and washings are passed through a column of 5 g of cationite, and the eluate and washings are titrated with 0.05 N NaOH , to give the Cl^- content of the sample.

R. TRUSCOE

1688. Quantitative analysis by infra-red spectroscopy. I. Determination of high purity γ -hexachlorocyclohexane by a compensating method. H. Kamada and S. Tanaka (*Japan Analyst*, 1953, 2 [2], 113-116).—The quant. analysis of small amounts of α - and δ -isomers in γ -hexachlorocyclohexane (I) by the use of their infra-red absorption spectra (12.58 μ for α , 13.22 μ for δ) is seriously affected by the absorption bands of the γ -isomer, especially when the purity of I is > 90 per cent.; therefore Daasch's method (*Brit. Abstr. C*, 1948, 93) cannot be carried out satisfactorily for them. This defect can be overcome by putting I (free from α - and δ -isomers) soln. (in CS_2) in the compensating optical path of the spectrometer. The working graph is linear in the range 5 to 20 mg per ml, but this method can be applied to a more dilute soln. by the use of the curved line below 5 mg per ml. The accuracy is discussed and found satisfactory for use in factory control.

K. SAITO

See also Abstracts 1462, 1522, 1528, 1546, 1571, 1692.

Agriculture and Plant Biochemistry

1689. Detection of E 605 [parathion]. J. Derkosch, H. Jansch, R. Leutner and F. X. Mayer (*Monatsh.*, 1954, 85 [3], 684-692).—Parathion (OO-diethyl O-p-nitrophenyl thiophosphate (I) or the corresponding OO-dimethyl compound (II) can be isolated from food residues or viscera by steam distillation. If the compound is present in large quantities it can be detected by examining the i.r. mol. vibration frequency of an ether extract of the steam distillate. Unlike u.v., the i.r. also allows distinction between I and II. Smaller quant. of parathion can be detected in the steam distillate itself by means of u.v. absorptiometry, but distinction between I and II cannot be made by this method. In a fatal case, the stomach contents revealed 0.29 mg per cent. of parathion; remains of unconsumed food contained 8.14 mg per cent.

P. HAAS

1690. The determination of nitrate and nitrite in soil. J. Buckett, W. D. Duffield and R. F. Milton (*Analyst*, 1955, 80, 141-145).—A critical investigation has been made of the various methods for

determining the small amounts of NO_3^- in soil; the 2:4-xylenol method, as modified by Barnes (*Brit. Abstr. C*, 1953, 94), was found most suitable. Nitrite is first determined independently and is then removed by treatment with urea. Procedure—The soil (5 g) is shaken with 20 ml of 10 per cent. acetic acid at 70°C for 3 to 5 min. and, after being set aside overnight, the extract is filtered. For the determination of NO_3^- , an aliquot of the extract is diluted to 8.4 ml with the acetic acid, 0.2 ml of dil. HCl (1 + 1) and 1 ml of 0.2 per cent. aq. sulphanilamide are added and, after 3 min., 0.2 ml of 0.5 per cent. aq. ammonium sulphamate. After 2 min., the colour is measured in a Spekker absorptiometer with a No. 6 blue-green filter. Finally, 0.2 ml of 0.5 per cent. N-1-naphthylethylenediamine dihydrochloride soln. is added and, after 3 min., the colour is measured as before. The reading is corrected for the first reading and for the reagent blank and then referred to a calibration graph prepared with standard NO_3^- soln. A 5-ml aliquot of the soil extract is treated with 0.5 ml of 10 per cent. urea soln. at 60°C for 3 min. and is then mixed with 15 ml of 80 per cent. H_2SO_4 , cooled and treated with 1 ml of 1 per cent. 2:4-xylenol in glacial acetic acid and maintained at 34°C for 30 min. The cooled mixture, after dilution with 80 ml of water, is extracted with 10 ml of toluene which, in turn, is extracted with 10 ml of 0.4 N NaOH . The optical density of the filtered alkaline extract is determined in a Spekker absorptiometer in u.v. light with a No. 7 blue filter. The calibration graph is prepared from standard NO_3^- solutions that have been submitted to the complete toluene extraction procedure.

A. O. JONES

1691. A rapid means of determining the pH of turbid pulps, using a colorimetric method. F. B. Michell (*Bull. Instn. Min. Metall.*, 1955, 64 [4], 1165-1168).—A brief investigation has been carried out on the use of barium sulphate as an aid to measuring the pH of turbid pulps by an adaptation of Kuhn's method of measuring the pH of soils. Tests with mine ores and ground minerals and the effect of dispersants on the rate of settlement are discussed. Under most conditions normally found in mineral dressing, the addition of barium sulphate produces sufficient clear liquor for the accurate colorimetric determination of the pH.

G. C. JONES

1692. Summary of the collaborative work on total nitrogen [in fertilisers]. Joint Committee of Ass. Off. Agric. Chem. and Amer. Oil Chem. Soc. (*J. Amer. Oil Chem. Soc.*, 1955, 32 [1], 35-36).—Certain variables in the method for determining total N in fertilisers and feeds are analysed statistically. Results indicate the superiority of Hg over Cu as a catalyst for the digestion of samples. There is no advantage in replacing standard acids by boric acid for the absorption of ammonia.

D. BAILEY

1693. A modification of the determination of phosphoric acid by the Lorenz method. H. Wiele (*Z. anal. Chem.*, 1955, 144 [6], 407-412).—In Lorenz's method for determining phosphoric acid in phosphates and fertilisers, the ultimate washing of the ppt. with dioxan instead of acetone affords pptn. of a more stable complex, which can be efficiently dried in an oven uninfluenced by higher temp., vacuum and suction times. The composition of the ppt. is determined, from which the P_2O_5 -content factor is deduced. Results accord with those of Lorenz's method, but provide a lower margin of error.

D. R. GLASSON

1694. **Modification of the *p*-anisidine method for the determination of free and total gossypol.** W. J. Miller (*J. Amer. Oil Chem. Soc.*, 1955, **32** [1], 29-33).

—A modification of the Pons and Guthrie method (*J. Amer. Oil Chem. Soc.*, 1949, **26**, 671) for determining free gossypol in cotton-seed materials is presented. Aniline is substituted for *p*-anisidine as the colour-producing reagent, and thus allows a blank determination to be used to correct for traces of dianilinogossypol (present in meals that are chemically treated to remove gossypol) extracted from the sample by the 70 per cent. aq. acetone. Increasing the reaction temp. for the aniline - gossypol reaction from 60° to 100° C gives a rapid and complete reaction with increased accuracy. The method is applicable to all types of cotton-seed meal. The method for total gossypol is also modified by doubling the strength of the oxalic acid used to hydrolyse bound gossypol and by using aniline to develop the colour.

D. BAILEY

See also Abstracts 1514, 1521.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

1695. **Apparatus for titrations in ultra-violet light.** K. P. Stolyarov (*Uch. Zap. Leningr. Gos. Un-ta*, 1953, [169], *Ser. Khim. N. No.* 13, 220-224; *Referativnyi Zh., Khim.*, 1954, Abstr. No. 36,392).—An apparatus for titrations in ultra-violet light is described. A filter with maximum transmission at 365 m μ is used, and the liquid to be titrated is contained in a beaker of ordinary glass.

E. HAYES

1696. **Studies on volumetric analysis by use of a high-frequency oscillator. III. Preparation of a portable titrimeter and its application.** M. Ishibashi, T. Fujinaga and M. Mitamura (*Japan Analyst*, 1953, **2** [3], 195-196).—A simple portable high-frequency titrimeter is prepared by use of IT4 valve and dry batteries (67.5 V and 1.5 V). The titration vessel is placed inside the condenser of the tank circuit and the change of impedance is measured by the change of the anode current of IT4. The whole size (except the burette) is about 25 cm \times 18 cm \times 14 cm and the stirrer is operated by clock-work. This apparatus is useful for work in the field. Several examples of neutralisation and precipitation titrations are shown.

K. SAITO

1697. **Apparatus for the preparation of chromatostrips.** J. M. Miller and J. G. Kirchner (*Anal. Chem.*, 1954, **26** [12], 2002).—An apparatus for coating glass strips with an adsorbent mixture such as starch - silicic acid is described.

D. R. GLASSON

1698. **Semi-automatic gas-separation equipment.** C. W. Hancher and K. Kammermeyer (*Anal. Chem.*, 1955, **27** [1], 83-87).—The operational and constructional details are described for an apparatus in which sampling, separation and determination of gases are carried out simultaneously and semi-automatically. The separation depends upon diffusion through a micro-porous membrane, e.g., porous glass. Results are given for He - O mixtures and are compared with those from normally operated equipment.

D. A. PANTONY

1699. **An isothermal distillation method for determining molecular weights.** C. E. Childs (*Anal.*

Chem., 1954, **26** [12], 1963-1964).—Signer's isothermal distillation method for determining mol. wt. (*Annalen*, 1930, **478**, 246) is further improved. Distillation is enhanced by including a reservoir of pure solvent in the system so that results within 5 per cent. of theoretical are obtainable in three days.

D. R. GLASSON

1700. **An improved Soxhlet extraction apparatus.** K. Schwarz (*Z. Lebensmittelforsch.*, 1954, **99** [6], 464-467).—The apparatus is figured and described. The return tube to the flask may be closed by a stopcock.

S.C.I. ABSTR.

1701. **Measurement of the viscosity of a liquid.** C. Brabender and C. W. Brabender, trading as Firma Brabender O.H. (*Brit. Pat.* 725,252, Date Appl. 12.8.53. *Ger. Pat.* 21.8.52 and 22.6.53).—The viscosity of the liquid is measured by recording automatically the time taken by a body of given sp. gr. to fall freely through the liquid. A vertical glass cylinder (for containing the liquid) has a solenoid wound around its lower end and disposed within it a body (provided with an iron ring) which can move freely. A time-recording instrument is operated as soon as the body begins to fall through the liquid and is stopped as soon as the iron ring enters the field of the solenoid.

J. M. JACOBS

1702. **New design of ultrafiltration apparatus.** R. Blum and G. L. Miller (*Science*, 1954, **120**, 669-671).—A new apparatus for the concn. of colloidal soln. by ultrafiltration that is suitable for large-scale work is described.

H. F. W. KIRKPATRICK

1703. **Sampling instruments.** H. Barker (*Studies in Conservation*, 1953, **1** [2], 82-83).—A diamond-tipped scraper for use in sampling museum objects has the diamond mounted in clear methacrylic plastic. This has an advantage over the normal method of mounting in hard or soft solder in that it avoids the chance of contaminating the prepared sample with traces of material that might cause confusion in a subsequent chemical or spectrographic analysis. A miniature sample collector, based on the principle of the cyclone separator, enables the detached sample to be transferred with a minimum of loss to a sample tube or microscope slide.

B. S. COOPER

1704. **New apparatus for measuring the resistance to ageing of lubricating oils.** B. Blouri (*Chim. et Ind.*, 1954, **72** [6], 1169-1174).—Samples of the oil are heated and agitated with air under standard conditions. The extent of the ageing is measured by the change in viscosity and by the increase in acidity.

G. SKIRROW

Optical

1705. **Scintillation spectrometer with improved response.** P. R. Bell (*Science*, 1954, **120**, 625-626).—A description is given of an improved scintillation counter that is claimed to be a step closer to the ideal gamma-ray spectrometer. The basis of the instrument is a large crystal of NaI that is equivalent to a sphere 5.25 in. in diam. and which replaces the cylinder (1.5 in. in diam., 1 in. high) of NaI activated by thallium in the ordinary counter.

H. F. W. KIRKPATRICK

1706. **Recording high-sensitivity paramagnetic resonance spectrometer.** J. M. Hirshon and C. K. Fraenkel (*Rev. Sci. Instrum.*, 1955, **26** [1], 34-41).—Details are given of a paramagnetic resonance absorption spectrometer operating at a wavelength

of 3.2 cm. The output signal of the spectrometer, which is of the crystal-heterodyne type, can be presented as a trace of the absorption *versus* field strength on a recorder, as an oscilloscope display of absorption *versus* field strength, or as a continuous recorder trace of the derivative of absorption *versus* field strength. The magnetic field is calibrated by means of the proton magnetic resonance absorption. Approx. 2×10^{-11} mole of 1:1-diphenyl-2-picrylhydrazine can be detected.

G. SKIRROW

1707. A non-polarising light modulator for the General Electric recording spectrophotometer. E. Atherton (*J. Opt. Soc. Amer.*, 1955, **45** [2], 130-131).—The use of a rotating-shutter modulator in place of a polarising prism has advantages when the spectral absorptions of anisotropic materials are measured, e.g., dyed viscose film. The shutter is in the form of a shallow metal cylinder with modulating sectors cut in the wall and positioned so as to be equivalent to a sector disc of infinite diameter.

B. S. COOPER

1708. Versatile anaerobic spectrophotometer cell. A. Lazarow and S. J. Cooperstein (*Science*, 1954, **120**, 674-675).—An anaerobic cell similar to the Thunberg tube, but which allows measurement of reaction rates in the Beckman model DU spectrophotometer, is described. H. F. W. KIRKPATRICK

1709. Beam-condensing system for Beckman IR-2 infra-red spectrophotometer. T. Y. Toribara (*Anal. Chem.*, 1954, **26** [12], 2003).—The beam-condensing system designed by Anderson and Miller (*J. Opt. Soc. Amer.*, 1953, **43**, 777) is installed in the Beckman IR-2 spectrophotometer, in a new section of transparent plastic inserted between the light-source compartment and the rest of the instrument. The light-source compartment may be separated for a considerable distance without loss in sensitivity, since the light beam is collimated. The spectrophotometer is thus easily adapted for handling micro-samples in pressed pellets of KBr. If the liquid-cell compartment is removed, an opening must be provided at the back of the lens compartment for introducing dry nitrogen.

D. R. GLASSON

1710. Improvements in or relating to cells for [infra-red] spectroscopy. The National Research Development Corporation [Inventor: A. C. Hughes] (Brit. Pat. 722,967; Date Appl. 28.8.53).—A cell for use in i.r. spectroscopy is described. A wall of the cell is moved by wedge-members operated with a knurled and graduated outer barrel. The screw thread on the cell body, on which the barrel moves, can be relatively coarse (20 to the inch), and the reduction of movement is effected by the angle of the bearing faces of the wedge-members.

E. J. H. BIRCH

Thermal

1711. Calorimetric determination of purity. Design and operation of a small adiabatic calorimeter. D. D. Tunnicliff and H. Stone (*Anal. Chem.*, 1955, **27** [1], 73-80).—An adiabatic calorimeter with attendant measuring circuits and operating instructions is described in detail. From the experimental results, the heat of fusion, m.p. of pure substance and m.p. of sample are determined, whence the purity of the sample is calculated with the use of standard formulae. Results are illustrated by reference to four hydrocarbons. The error for samples of > 99.8 mole per cent. purity is given as < 0.05 mole per cent.

D. A. PANTONY

Electrical

1712. Micro-electrolytic apparatus. British Standards Institution (B.S. 1428: Part J1: 1954, 8 pp.).—Platinum electrodes of the Lindsey-Sand type are specified, and a suitable electrolysis vessel with a frame for their support is described.

D. R. GLASSON

1713. Modified electrophoretic vessels. V. Kalous (*Chem. Listy*, 1954, **48** [5], 771-773).—Two silver chloride electrode vessels, each constructed of an S-shaped glass tube (25 mm in diameter and 500 ml in volume), are connected by broad rubber tubing to two ground points inserted in a Perspex disc (3 cm thick), forming the upper part of a rectangular optical cell. The vessels are readily constructed, filled and cleaned. They are suitable for routine electrophoretic analyses of such materials as blood serum and plasma.

G. GLASER

1714. New electrophoresis cell for dual analysis. H. Corey and I. Oreskes (*Science*, 1954, **120**, 675-676).—A dual-analysis electrophoresis cell is described which permits duplicate ascending or descending patterns to be obtained for each sample.

H. F. W. KIRKPATRICK

1715. Power supplies for electrophoresis apparatus. W. J. Perkins (*Lab. Practice*, 1955, **4** [3], 117-118).—Constant-current and constant-voltage circuits, with sufficient stabilisation to use in electrophoresis apparatus, are described. A combined circuit with two pentodes which gives both constant voltage and constant current is also described.

E. J. H. BIRCH

1716. Polarography with a vibrating platinum micro-electrode. W. Dirscherl and K. Otto (*Chem.-Ing.-Tech.*, 1954, **26** [6], 321-324).—A vibrating platinum electrode for the continuous estimation of oxygen in water is described. A vertical steel strip is clamped at the top and joined to an insulated steel wire, which projects through an insulating cap into the cell and carries the platinum electrode, which is 1 to 2 mm. long. The strip is vibrated at variable amplitude at 50 c.p.s. by an electromagnet. The cell is separated by a porous diaphragm from a N calomel electrode. The diffusion current varies as the square root of the amplitude, and is greater than with the rotating electrode (up to 120 μ A). Slight differences are observed between the ascending and descending wave. In 0.1 N NaOH, but not at pH 10, there is a min. at the top of the wave at -1.1 V, attributed to discharge of H⁺. This can be avoided by the addition of 0.01 N NaCN, which displaces the wave. Repeated measurements on the same sample give continuously lower waves owing to consumption of oxygen.

A. B. DENSHAM

1717. A new-type mercury electrode for polarography. Y. Yashiro (*Bull. Chem. Soc. Japan*, 1954, **27** [8], 564).—The electrode described has a pin-hole small enough to prevent mercury, kept at constant-pressure level, falling through it. A sensitivity comparable with that of the dropping-mercury electrode is obtained, the polarograms being very smooth with less slope than those for the Heyrovský-Foréjet streaming-mercury electrode. Residual currents ($\approx 0.05 \mu$ A at -0.6 V) are almost completely eliminated when a pair of electrodes of the same characteristics are used in a polarographic circuit, e.g., in oscillographic, derivative and differential or potentiometric plot polarography or in amperometry.

D. R. GLASSON

sh Stan-
8 pp.).—
type are
with a
LASSON
Kalous
o silver
d of an
500 ml
tubing
ex disc
angular
ructed,
routine
s blood
ASER

analysis.
D, 675-
ell is
ing or
sample.
RICK

ppara-
l, 117-
ge cir-
electro-
nbined
nstant
l.
RCH

tinum
Chem-
rating
ion of
l strip
ulated
ng cap
trode,
ted at
agnet.
rom a
varies
reater
(μ A).
scen-
, but
wave
This
aCN,
sure-
lower

AM
laro-
1954,
-hole
ant-
ivity
elec-
ooth
ky-
dual
com-
the
phic
ffer-
r in
ON

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	millicurie	mC
ampere	amp.	milligram	mg
Angstrom unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicron	m μ
aqueous	aq.	millivolt	mV
atmosphere, -ic	atm.	minimum	min.
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul -e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	number	no.
coefficient	coeff.	observed	(obs.)
concentrated	conc.	ounce	oz
concentration	concn.	part	pt.
critical	crit.	patent	pat.
crystalline	{ cryst.	parts per million	p.p.m.
crystallised	cryst.	per cent. wt. in wt.	per cent. w/w
cubic	cu.	per cent. wt. in vol.	per cent. w/v
current density	c.d.	per cent. vol. in vol.	per cent. v/v
cycles per second	c.p.s.	potential difference	p.d.
decompos -ing, -ition	(decomp.)	pound	lb
density	ρ	precipitate	ppt.
density, relative	d or wt. per ml	precipitated	pptd.
derivative	deriv.	precipitating	pptg.
dilute	dil.	precipitation	pptn.
direct current	d.c.	preparation	prep.
distilled	dist.	qualitative, -ly	qual.
electromotive force	e.m.f.	quantitative, -ly	quant.
electron-volt	eV	recrystallised	recryst.
equivalent	equiv.	refractive index	n_D
experiment	expt.	relative humidity	R.H.
foot, feet	ft.	revolutions per minute	r.p.m.
gram	g	saponification value	sap. val.
gram-molecule	mole	saturated calomel electrode	S.C.E.
half-wave potential	$E_{\frac{1}{2}}$	second (time)	sec.
horse-power	h.p.	soluble	sol.
hour	hr.	solution	soln.
hydrogen ion concentration	[H ⁺]	specific gravity	sp. gr.
hydrogen ion exponent	pH	specific rotation	[α]
inch	in.	square centimetre	sq. cm
infra-red	i.r.	standard temperature and	
insoluble	insol.	pressure	s.t.p.
kilogram	kg	temperature	temp.
kilovolt	kV	ultra-violet	u.v.
kilowatt	kW	vapour density	v.d.
maxim -um, -a	max.	vapour pressure	v.p.
melting-point	m.p.	volt	V
microcurie	μ C	volume	vol.
microgram	μ g	watt	W
microlitre	μ l	wavelength	λ
micron	μ	weight	wt.
milliampere	mA		

In addition the following symbols are used—

greater than	>	less than	<
not greater than	\nlessgtr	not less than	\nlessgtr
is proportional to	\propto	of the order of, approximately	\approx

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, e.g., Cu⁺⁺, Al⁺⁺⁺, Cl⁻, SO₄⁼⁻. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, e.g., ferric iron becomes Fe^{III} and cuprous copper Cu^I.

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: R. C. Chirnside.
Members: B. S. Cooper, B. A. Ellis, D. C. Garratt, I. MacIntyre, B. J. Walby, W. A. Waygood
and the President and Honorary Officers

President of the Society: K. A. Williams

Hon. Secretary of the Society:
N. L. Allport

Hon. Assistant Secretary of the Society:
R. E. Stuckey

Hon. Treasurer of the Society:
J. H. Hamence

Editor: Norman Evers, B.Sc., Ph.D., F.R.I.C.

Assistant Editor: Mrs. H. I. Fisk, B.Sc.

CONTENTS

									Abstract
General Analytical Chemistry	1426
Inorganic Analysis	1447
Organic Analysis	1548
Biochemistry									
Blood, Bile, Urine, etc.	1602
Drugs	1641
Food	1662
Sanitation	1686
Agriculture and Plant Biochemistry	1689
General Technique and Laboratory Apparatus									
General	1695
Optical	1705
Thermal	1711
Electrical	1712

Printed and Published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England.
Communications to be addressed to the Editor, Norman Evers, 20, Eastcheap, London, E.C.3. Enquiries
about advertisements should be addressed to Walter Judd Ltd., 47, Gresham Street, London, E.C.2.

Entered as Second Class at New York, U.S.A., Post Office

55

y:

act

426

447

548

602

641

662

686

689

695

705

711

712

land.
series